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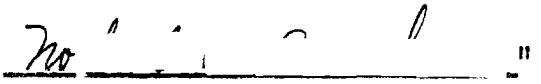

THE KINETICS OF THE BASE-CATALYZED DEUTERIUM EXCHANGE OF SOME HALOFORMS IN AQUEOUS SOLUTION

A THESIS

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the Faculty of the Graduate Division

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Doctor of Philosophy in the School

of Chemistry

By

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THE KINETICS OF THE BASE-CATALYZED DEUTERIUM EXCHANGE OF SOME HALOFORMS IN AQUEOUS SOLUTION

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ABSTRACT

The first extensive investigation on the basic hydrolysis of haloforms was made by Hine, Dowell and Singley[1]. Evidence presented showed that the alkaline hydrolysis of haloforms probably proceeds by the mechanism

$$CHX_3 + OH^- \underset{\text{fast}}{\rightleftharpoons} CX_3^- + H_2O$$

$$CX_3^- \xrightarrow{\text{slow}} X^- + CX_2$$

$$CX_2 \xrightarrow[H_2O]{OH^-,\ \text{fast}} CO + HCO_2^-$$

where X is any halogen.

Hine, Peek and Oakes[2] had studied the rate of the base-catalyzed deuterium exchange for chloroform as part of the study of the relative importance of inductive and resonance effects on acidity and also in relation to the mechanism of the basic hydrolysis of haloforms. In order to rational-

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(1) J. Hine, A. M. Dowell, Jr. and J. E. Singley, Jr., J. Am. Chem. Soc., 78, 479 (1956).

(2) J. Hine, R. C. Peek, Jr. and B. D. Oakes, ibid., 76, 827 (1954).

ize the data on the relative reactivities of haloforms toward basic hydrolysis as well as to further add to our general knowledge of the effect of structure on reactivity in carbanion formation, the effect of various halogen atoms on the ease of removal by base of hydrogen atoms attached to the same carbon atom was studied in this program.

The kinetics of the base-catalyzed deuterium exchange of dichlorofluoromethane, dichloroiodomethane, dibromochloromethane and bromochlorofluoromethane in aqueous solution were studied by infrared measurement of the isotopic content of the haloform.

$$CDX_3 + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CX_3^- + HOD$$

$$CHX_3 + OH^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} CX_3^- + H_2O$$

By studying the above four haloforms and comparing their rate constants for exchange with other existent exchange data, it was felt that much of the necessary knowledge needed to compare the effects of α-halogens on haloforms in exchange reactions would be available. The alkaline hydrolysis and base-catalyzed deuterium exchange of dichlorofluoromethane were studied at 0 and 20^o and 0 and 15^o for

bromochlorofluoromethane. The base-catalyzed deuterium exchange of dichloroiodomethane and dibromochloromethane was studied at 0 and 35°. Kinetic equations were derived to take into account the complication of concomitant hydrolysis during the deuterium exchange reaction for the two fluorohaloform compounds. The kinetic isotope effect for carbanion formation was measured for the fluoro-haloform compounds. The deuterium exchange of the other two haloforms was found to be pseudounimolecular since hydrolysis was negligible during the main course of exchange and the equation derived for the study of chloroform was used. Heats and entropies of activation were calculated.

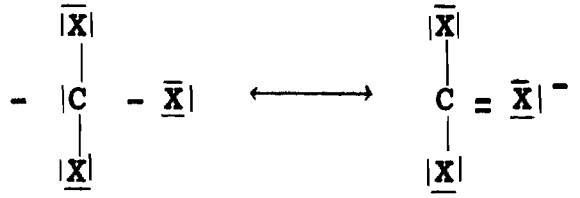
The possibility of general base catalysis was investigated by the use of an ammonia-ammonium perchlorate buffer. It was believed that general base catalysis was demonstrated but the values reported were obtained from a small difference between two large numbers.

Attempts were made to prepare pure deuterofluoroform in order to measure its exchange rate. The method used was unsuccessful.

The rate constants for deuterium removal in basic aqueous solutions of the four haloforms measured along with the rate constants which were available for five other halo-

forms indicated the following order of reactivity: $CDI_3 \sim CDBr_3 > CDBr_2Cl > CDBrCl_2 \sim CDCl_2I > CDBr_2F > CDCl_3 > CDBrClF > CDCl_2F$. An approximation of the exchange rate constant for deuterofluoroform placed this haloform very far below deuterodichlorofluoromethane in reactivity.

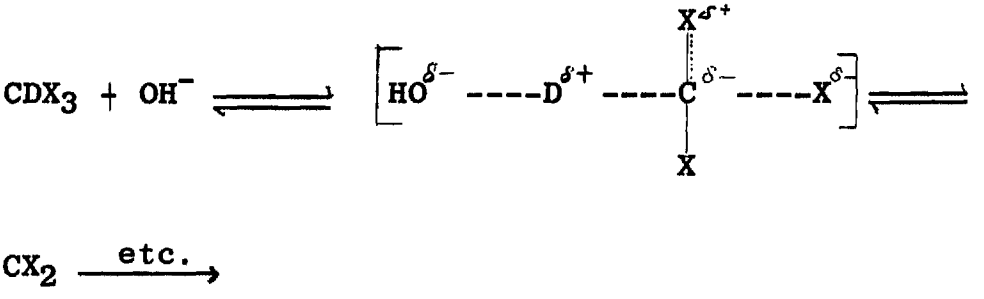
The reaction rate constants of these nine haloforms and their implication are discussed in terms of steric factors (B-strain), inductive effects (I_s), inductomeric polarizability (I_d) and the stabilization of the carbanion like transition state by the contribution of structures with ten electrons in the outer shell of a halogen, i.e., d-orbital resonance



where X is any halogen. An analysis of data indicated that the steric effect (B-strain) should contribute only slightly (15 per cent or less) to the reactivity of a haloform and it was questionable whether d-orbital resonance was a reality or if the differences in the rate constants might be due only to the I_d effect. Any contribution to reactivity that might be attributed to d-orbital resonance can also be explained

alone by the I_d effect. Although the I_s effect seemed to be smaller than d-orbital resonance or the I_d effect, no evidence was present to indicate its actual importance in deuterium or protium ion removal.

Since haloforms containing one or two fluorine atoms show concomitant hydrolysis during exchange, the possibility of a concerted attack by a hydroxide ion is discussed. The attack could take place by the following general mechanism:



A comparison of the rates of carbanion formation by two different routes for four haloforms and four other compounds was made. A straight line relationship is shown for six of the eight compounds. A relationship between the effects of halogens on the rate of deuterium removal was also attempted. Three curves are shown and can be used to predict rate constants for deuterium removal for other haloforms.

The isotope effect for dichlorofluoromethane and bromochlorofluoromethane showed that hydroxide ions remove protons from these haloforms only about 50-75 per cent

faster than they remove deuterons. The isotope effect was found to vary with temperature (k_1/k_2 increases with increasing temperature).

A brief summary of kinetic data at 0° for deuterium exchange, heats and entropies of activation are listed in the following table:

Summary of Kinetic Data on Carbanion Formation by Haloforms in Aqueous Solution.

Haloform	10^4 k_1 at 0.0°	$\Delta H^{\ddagger}$ (kcal.)	$\Delta s^{\ddagger}$ (e.u.)
$CDCl_2F$	$0.893 \pm .018$	$25.9 \pm .6$	17.7 ± 2.3
$CDCl_2I$	275 ± 5	$22.1 \pm .2$	$15.3 \pm .6$
$CDBr_2Cl$	1435.0 ± 15.8	$21.3 \pm .2$	$15.6 \pm .6$
$CDBrClF$	$21.0 \pm .5$	$24.3 \pm .5$	18.4 ± 1.7

CHAPTER I

INTRODUCTION

Previous workers[1] have studied the hydrolysis of various haloforms in order to investigate further the mechanism by which they react and to study the effect of structure on reactivity. Certain anomalies which need further explanation were found to exist. One of these is that bromochlorofluoromethane has the largest rate of hydrolysis for the haloforms studied. This does not seem reasonable if the rates for hydrolysis are considered in terms of ease of carbanion formation since bromochlorofluoromethane is not expected to form as stable (d-orbital resonance) a carbanion as some of the other haloforms studied.

Hine, Peek and Oakes[2] studied the kinetics of the base-catalyzed deuterium exchange of chloroform and substantiated work by Horiuti and Sakamoto[3] that exchange takes place more rapidly than basic hydrolysis.

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(1) J. Hine, A. M. Dowell, Jr. and J. E. Singley, Jr., J. Am. Chem. Soc., 78, 479 (1956).

(2) J. Hine, R. C. Peek, Jr. and B. D. Oakes, ibid., 76, 827 (1954).

Therefore, the study of exchange rates should aid in rationalizing any anomalies arising from hydrolysis studies along with adding to our knowledge of the effect of structure on reactivity in carbanion formation. By proper choice of haloforms the relative effects of α-halogens on the ease of carbanion formation can be studied.

By studying dichlorofluoromethane, dichloroiodomethane, dibromochloromethane and bromochlorofluoromethane and comparing their rate constants for exchange with other existent exchange data, most of the knowledge necessary to compare the effects of α-halogens on haloforms in exchange reactions is made available.

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(3) Y. Sakamoto, J. Chem. Soc. Japan, 57, 1169 (1936); J. Horiuti and Y. Sakamoto, Bull. Chem. Soc. Japan, 11, 627 (1936).

CHAPTER II

EXPERIMENTAL

Kinetic Runs

General.--The kinetic runs at 15, 20.2, 20.35 and 35° were made in a large constant temperature bath. All temperatures were believed constant within 0.05°. The bath thermometers (graduated to 0.1°) were checked against a thermometer calibrated by the Bureau of Standards and the recorded temperatures were accurate to within 0.1°. In order to maintain temperatures of 15, 20.2 and 20.35°, it was necessary to circulate refrigerated ethylene glycol through coils in the bath. All runs at 0° were kept in one-gallon Dewar flasks containing an ice-water slurry and the Dewar flasks were kept in an ice box maintained at approximately 8°. A multiple flask technique and oxygen-free distilled water were used in all runs. Zero times were taken when the pipette of added base was half emptied and after reaction initiation with base, each flask was taken out of the bath and was shaken by hand for approximately 20 seconds. The flasks were then quickly returned to the Dewar flask. Appendix 1 summarizes all kinetic runs, and hydrolysis and exchange rates.

Dichlorofluoromethane.--The general procedure for basic hydrolysis and exchange runs of dichlorofluoromethane at 0° was to pipette out under a nitrogen atmosphere 90 ml. of water near 0° into each of several 100-ml. volumetric flasks. The flasks were weighed on an analytical balance and then cooled in the freezing compartment of a refrigerator. About 0.3 g. of cold dichlorofluoromethane was syringed under nitrogen into each flask. The flasks were shaken mechanically until all of the haloform had dissolved. The exterior of the flasks were rinsed with distilled water and then with methanol and allowed to dry. Each flask was reweighed accurately, then allowed to sit for several hours and after opening the flask to the atmosphere for about one minute to lower the haloform vapor concentration above the solution's surface (insure against a saturated solution and that all haloform had dissolved), they were again reweighed. This procedure was repeated until weights constant to within 0.9 mg. were obtained. The flasks were placed in a 0° bath for several hours and examined for the presence of the crystalline haloform hydrate that forms if the solutions are too concentrated and allowed to stand too long[1].

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(1) W. P. Banks, B. O. Heston, and F. F. Blankenship, J. Phys. Chem., 58, 962 (1954).

After thermostating for at least two hours, the reactions were initiated by pipetting into each flask standard sodium hydroxide at near bath temperature. The reactions were stopped by pouring the contents of the flask into cold standard acid and the interiors of the flasks were rinsed with distilled water. The solutions were back-titrated with standard base using phenolphthalein indicator with the haloform solution kept at 0-5^{o} in an ice bath to diminish the loss of the volatile haloform when the base at room temperature was added. Blanks were made on each run. The final volume for each flask was 100 ml. at the reaction temperature.

Difficulty was encountered in back-titrating the haloform solutions of the exchange runs. The indicator end point was obtained for a 20-30 second period but about 0.1 ml. of additional base was necessary for a persistent pink color. Each exchange solution was then extracted with four 10 ml. portions of cold carbon disulfide which were combined, dried over a minimal amount of indicating silica gel, diluted to the necessary concentration, and analyzed for dichlorofluoromethane and deuterodichlorofluoromethane.

For the basic hydrolysis and exchange runs of dichlorofluoromethane at 20.2 and 20.35^{o} lower haloform and base concentrations were used. The general procedure for the

preparation of standard haloform solutions was the same as for the runs at 0° but the distilled water was measured at room temperature. Run B was made at 20.35° using 95 ml. of haloform solution in water, while runs D, E, EA, EB and F at 20.2° used 90 ml. of such solution in 100-ml. volumetric flasks. The total volume of each sample in a run was 100 ml. at reaction temperature.

Table 1. Runs with Dichlorofluoromethane at 0, 20.2 and 20.35°.

	Base		Acid	
Run	ml.	N	ml.	N
A	10	0.3096	a	
C	10	0.1700	a	
EB	10	0.1700	20	0.1090[b]
B	5	0.1400	10	0.1090[a]
D	10	0.0658	10	0.1090[a]
E	10	0.0696	10	0.1032[a]
F	10	0.0696	10	0.1032[a]
EA	10	0.0696	10	0.1032[b]
EG	10	0.0562	8	0.1034[b]

[a]See tables in appendix 1 for additional data on acid and back-titration (blank).

[b]Used initiatory base to back-titrate.

Each exchange solution was extracted with four 2 ml. portions of cold carbon disulfide and the same procedure that was used at 0° was followed. Table 1 lists the volumes and concentrations of the initiating base and

arresting acid for all runs with dichlorofluoromethane.

Dichloroiodomethane.--Run EI at 0^{o} and run EJ at 35^{o} for the deuterium exchange of dichloroiodomethane were made in 100-ml. low-actinic volumetric flasks. The flasks were flushed with nitrogen, and 80 ml. of water and 0.1 ml. of 0.1310 N perchloric acid were pipetted into the flasks at 21 and 22^{o} respectively. After approximately 0.08 ml. of 85.1 per cent deuterodichloroiodomethane was syringed into each flask, it was shaken mechanically for 20 minutes and checked to see that all of the haloform had dissolved. The flasks were placed in the bath for at least twelve hours for run EI and about five hours for run EJ. Each flask was initiated by adding 10 ml. of a buffer solution at reaction temperature as shown in table 2. All points were stopped with 4 ml. samples of 1.1459 N perchloric acid, extracted with two 3 ml. portions of isooctane and stored in black painted flasks until analyzed for isotopic concentrations. All operations were carried out under nitrogen whenever possible. Several of the extracted aqueous solutions were tested for the presence of halide ions with several ml. of a 1 N silver nitrate solution. No turbidity was noted indicating little or no hydrolysis took place during exchange. Calculations for maximum time of exchange at 35^{o}, using a rate constant

of 12.654×10^{-4}, showed that less than 0.02 per cent haloform had hydrolyzed.[2] The initial 0.1 ml. of 0.1316 N perchloric acid was used to lower the initial hydroxide concentration to suppress possible deuterium exchange before the desired commencement of reaction.

Table 2. Runs with Dichloroiodomethane and Dibromochloromethane at 0° and 35°.

Run[a]	Buffer. $[NH_3]$	$[NH_4ClO_4]$	$[NaClO_4]$	Final Volume[b]
EI	0.2541	0.3959		89.95
EI	0.0991	0.1545	0.24	89.95
EJ	0.2526	0.3936		90.42
EJ	0.0986	0.1536	0.24	90.42
EK	0.2499	0.3965		89.83
EK	0.0962	0.1547	0.24	89.83
EL	0.2484	0.3942		90.30
EL	0.0956	0.1538	0.24	90.30

[a]Each run represents a five flask (point) run.

[b]Assumed ideal partial molar volumes. Initial measured volumes of water were extrapolated to reaction temperature.

Dibromochloromethane.--The kinetic deuterium exchange runs (EK at 0° and EL at 35°) on this compound were carried out

(2) A. M. Dowell, Jr., "The Mechanism of the Basic Hydrolysis of Haloforms," Unpublished Ph. D. Thesis, Georgia Institute of Technology, 1954, p. 76.

in a manner similar to those for dichloroiodomethane with the following exceptions. The wafer was pipetted at 27° and ~0.07 ml. of 93.0 per cent deuterodibromochloromethane was used for each point. Ten ml. samples of 1.1459 N perchloric acid were used to arrest the reaction mixtures and extractions were not carried out under nitrogen. Table 2 shows the buffer concentrations and final volumes; tables in appendix 1 list final kinetic data.

Bromochlorofluoromethane.--Bromochlorofluoromethane solutions for runs O and EQ at 0° and M, N, and ER at 15° for aqueous basic hydrolysis and exchange were prepared by pipetting 80 ml. of water and 0.2 ml. of 0.1316 N perchloric acid (run M contained 0.1 ml.) into 100-ml. volumetric flasks at 23-25°. For run M between 0.08 and 0.1 ml. of haloform was syringed into each flask while run N contained about 0.05 ml., run O about 0.06 ml., and run P 0.07 ml. of protohaloform. Runs EQ and ER contained 0.05-0.08 ml. of haloform which was 95.9 per cent deuterobromochlorofluoromethane. All standard bromochlorofluoromethane solutions were prepared using an analytical balance before and after adding haloform. The solutions were shaken mechanically until all haloform had dissolved. Each flask was initiated with standard sodium hydroxide at the approximate bath temperature. Sam-

ples in runs M, N, O, P and EQ were stopped by adding to each flask standard perchloric acid while run ER was stopped by pouring the haloform solutions into cold standard perchloric acid and rinsing the flask with distilled water. All samples were back-titrated (solutions at 0-5°) to a blue-green intermediate end point with standard sodium hydroxide using ten drops of bromothymol blue as indicator. This indicator with a pK of approximately 7 was used in order to prevent further exchange and hydrolysis while back-titrating. The runs at 15° were made with room temperature near 20° in order to minimize temperature errors while pipetting samples and taking the haloform samples from the temperature bath in order to shake. Total volume for each sample in runs M and N was 94.96 ml. and 90.06 ml. respectively at 15° while samples in runs O and P were 90.00 ml. Samples in run EQ had a final volume of 94.98 ml. each at 0° while those in run ER contained 92.07 ml. each at 15°. These volumes were calculated on the assumption that partial molal volumes were ideal and that the volume-temperature relationship was the same as for pure water. Each haloform solution in run EQ was extracted with two 2 ml. portions of isooctane while samples in run ER were extracted with two 3 ml. portions of isooctane. Each sample was dried with a minimal amount of

silica gel and then analyzed. Table 3 list the volumes and concentrations of the initiating base and arresting acid used for all runs with bromochlorofluoromethane.

Table 3. Runs with Bromochlorofluoromethane at 0 and 15°.

Run	Base		Acid	
	ml.	N	ml.	N
O	10	0.0521	a	
P	10	.1102	a	
EQ	15	.1102	15	.1316[b]
M	15	.0656	a	
N	10	.0656	a	
ER	12	.0678	6	.1316[c]

[a]See tables in appendix 1 for data on acid and back-titrations (blank).

[b]Back-titrated with 0.1099 N NaOH.

[c]Back-titrated with 0.06763 NaOH.

Fluoroform.--Two runs were attempted for the basic decomposition of fluoroform. In the first run six 25-ml. flasks, each of which contained 10 ml. of 0.04654 M fluoroform in t-amyl alcohol, were initiated with 10 ml. of 0.1075 N potassium t-amyloxide and diluted to 25 ml. with t-amyl alcohol at 28.85°. The solutions were 0.01862 M in fluoroform and 0.0430 N in potassium t-amyloxide at 28.85°. The

reactions were stopped by pouring into 12 ml. of 0.1086 N hydrochloric acid and back-titrating with 0.02746 N sodium hydroxide using phenolphthalein indicator. It was impossible to see the end point.

In the second run each of seven 15 ml. samples of 0.0801 N potassium t-amyloxide was mixed after thermal equilibrium with a 10 ml. sample of 0.0521 M fluoroform in t-amyl alcohol at 28.88°. Five of the reaction mixtures (at 28.88°C) were stopped between one and two thousand minutes by pouring each one into a mixture of 1 ml. of 0.1090 N hydrochloric acid and 50 ml. of methanol. The mixtures were back-titrated with 0.0275 N sodium hydroxide using 30 drops of a solution of 0.5 per cent by weight of curcumine in a 50 per cent methanol-water solution as an indicator. Indications were that there was no hydrolysis taking place and one sample which had been allowed to go for one week was analyzed for the presence of fluoride ion. The results indicated that none was present in solution.

Isotopic Analysis

The deuterohaloforms were analyzed by infrared measurements using a Perkin-Elmer Model 21 instrument. The spectra were first run for the different haloforms using various solvents. Also, the spectra were run neat. Then the solvent

which obliterated the least number of major absorption bands and could be favorably used in preparing standard haloform solutions along with being capable of extracting the haloform was used. Isooctane was best suited for all haloforms run except dichlorofluoromethane in which case carbon disulfide, which is less favorable for the preparation of standard solutions, was used as the solvent.

The general procedure was to try to find at least two major absorption maxima each for the deuterohaloform and protohaloform. The wave lengths of these maxima were then determined as accurately as possible by setting the drum ratio to the cam drive at 40:1, setting the wave length slightly below the absorption maximum and allowing the wave length drive to move very slowly. Because of the 40:1 ratio, instead of a sharp point, a plateau was obtained, the midpoint of which was taken as the absorption maximum. This was repeated at various concentrations which gave measurements at approximate optical densities between 0.1 and 1. The maximum absorption bands which varied approximately $\pm$ 0.002 were then averaged and the value obtained was used as the band of maximum absorption. The slit widths for all bands were noted at an approximate resolution control of 965. Figures 4-7 in appendix 2 compare the proto- and

deuterohaloforms that were investigated.

Standard solutions of protohaloforms in their solvents were prepared. Standard carbon disulfide - dichlorofluoromethane solutions were obtained by preparing thin-walled glass vials of weighed haloform and these vials were broken into a measured amount of cold carbon disulfide. The carbon disulfide was cooled by surrounding the flask with finely divided dry ice. All other attempted methods for preparing standard carbon disulfide solutions gave very erratic molecular extinction coefficients.

With the standard protohaloform solutions, optical densities were measured at all the determined bands using a 0.051 cm. sodium chloride solution cell and a 0.0506 cm. sodium chloride solvent cell. Various concentrations of haloform were used at a given band to see if the Beer-Lambert law held over the range of 0.2-.6 optical density. The extinction coefficients, which are "apparent" since they were determined from the optical density of a standard solution compared with pure solvent in the same cell, were determined using the following equation

$$\epsilon = \frac{O.D.}{l \times c}$$

Where ϵ is the molecular extinction coefficient, O.D. is

the optical density, $\underline{l}$ is length of cell and $\underline{c}$ is the molar concentration of haloform solution. The optical densities were measured directly on "optical density" paper. The negative protium molar extinction coefficients obtained at the various deuterium bands were obtained when the solvent absorbed more strongly than the protium haloform.

The molar solvent extinction coefficients were measured at the various protium bands. This was accomplished by initially setting the infrared machine with the solvent and sample cell pair containing only solvent at a given protium band. Then the sample cell only was replaced with various size cells containing solvent only and the optical densities were measured. The difference between the initial sample cell and its replacement cell according to length, the measured optical density and the known molar concentration of the solvent were used to calculate the molar extinction coefficient for the solvent at a given protium band.

The "apparent" molar extinction coefficients for the deuterohaloforms at the protium bands were determined using molar solvent extinction coefficients. The molar solvent extinction coefficient was multiplied by the liter per mole ratio of molar volumes of haloform to solvent to give the "apparent" molar extinction coefficients for the deutero-

haloform at the protium band. The value was negative, since the deuterohaloform was considered not to absorb at the protium band and to give an "apparent" negative absorption by displacing some of the solvent which does absorb. It was necessary to assume that the deuterohaloform did not absorb since no isotopically pure material was present to show otherwise. Table 25 in appendix 1 summarizes the apparent molecular extinction coefficients for the haloforms.

Since no pure deuterohaloform had been prepared, it was necessary to find the per cent of deuterohaloform present in the mixture. Concentrated standard solutions of unknown isotopic percentage were prepared and their optical densities were determined at the protium bands. Due to the small protium concentration in the mixture, it was necessary to prepare concentrated standard solutions, in order to obtain optical densities of 0.2 or more. However, the deuterohaloform's presence made it necessary to use the following equations

$$\text{(i)}\quad \frac{\text{O.D.}_{\text{total}}}{[CDX_3]} = \epsilon^{H}_{H} \times 1 \times [CHX_3] + \epsilon^{H}_{D} \times 1 \times \qquad (1)$$

$$\text{(ii)}\quad \text{if } C_{\text{total}} - [CHX_3] = [CDX_3]$$

$$\text{(ii)}\quad \text{O.D.}_{\text{total}} = \epsilon^{H}_{H} \times 1 \times [CHX_3] + \epsilon^{D}_{D} \times 1 \times [C_{\text{total}} - (CHX_3)]$$

where $O.D._{total}$ is the optical density measured at the protium band, ϵ_H^H and ϵ_D^D are "apparent" molecular extinction coefficients for the protohaloform, and the deuterohaloform at the protium band, $\underline{l}$ is the length of cell used, $[CDX_3]$ and $[CHX_3]$ are the concentrations of the deuterohaloform and protohaloform and C_{total} is the over-all concentration in haloform prepared.

With C_{total}, ϵ_H and ϵ_D known and $O.D._{total}$ measured, $[CHX_3]$ and then $[CDX_3]$ can be calculated and thus, the per cent of deuterohaloform present is obtained. With this information more standard mixed isotopic haloform solutions were prepared and the "apparent" molar extinction coefficients were determined at the deuterium band for the deuterohaloforms using (1i). Since the D_{total} can be measured and $[CHX_3]$ and $[CDX_3]$ are known along with ϵ_H^D (the extinction coefficient for the protohaloform at the deuterium band), then the ϵ_D^D of the deuterium band can be determined. With the molar "apparent" extinction coefficients known at all bands for the protohaloform and deuterohaloform, all information needed for analysis was present.

The following general procedure was used for optical density determinations with dichloroiodomethane, dibromochloromethane and bromochlorofluoromethane. After the mach-

ine had been set at each of the protium and deuterium bands for the given haloform with the solvent and solution cells containing solvent only, the solution cell was then filled with a sample of extracted haloform for a run. Optical densities were then measured at all the major bands for each sample without resetting the machine when a measurement was made at the next band. Thus, the possible concentration changes through volatilization while changing solutions at each band were eliminated. From these optical densities for each point and the known extinction coefficients at each band, the protium and deuterium contents were obtained.

The general procedure for dichlorofluoromethane differed from the above method of measurement in that it was necessary to reset the machine at each band measured. Therefore, it was necessary to empty and refill the solution cell with the sample at each band measured.

The calculations of the isotopic content varies somewhat with each compound measured. For dichlorofluoromethane the extinction coefficient at the 12.635μ band for deuterodichlorofluoromethane was negligible and therefore the concentration of the protium compound for each point could be calculated directly. These concentrations were substituted in

(li) along with the measured optical densities at the two deuterium bands and the previously calculated protium and deuterium extinction coeffficients to calculate the deuterium concentration for each point. The two deuterium concentrations for a point were averaged and these values were used to calculate the protium concentrations at the mixed protium-deuterium band at 9.415 μ. This value was used only as a check on the lone protium band.

For dichloroiodomethane and dibromochloromethane, the method was slightly more complex. A band which had the smallest extinction coefficient was chosen for each haloform. The smaller of the two coefficients for that band was ignored and the approximate haloform concentration (either protium or deuterium) was calculated for each point of a run. Then the measured optical densities and the two known molar extinction coefficients at the two isotope bands along with the approximate haloform concentrations were substituted in (li). The one isotope haloform concentration was calculated at the two bands and averaged. These values were then used to recalculate the original approximated isotope's concentration accurately at its two bands and these values were averaged.

The method of isotopic calculations was the simplest

for bromochlorofluoromethane. This haloform had two deuterium bands which had very small $\epsilon \frac{D}{H}$ values and one protium band whose $\epsilon \frac{H}{D}$ value was very small. These were considered negligible and the isotopic concentrations were calculated without any approximations first being made. An attempt was also made to use the mixed protium and deuterium band at 9.399μ to check the protium concentrations measured at 12.882μ but the check was poor.

Whenever possible the concentrations of the various extracted solutions were so made up that optical densities between 0.2 and 0.6 were obtained. In cases where measurements at two protium or two deuterium bands gave one measurement in the 0.2-0.6 range and one outside of it, the optical density in this range was used and the other value was used only as a check. When both values were in this range, the two concentrations were averaged. In the small number of cases where both measurements were not in the range, then both concentrations were averaged together and used.

Equation for Basic Hydrolysis

The second order rate constants for basic hydrolysis of protohaloforms were calculated using the following intergrated equation[3]

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(3) J. Hine, J. Am. Chem. Soc., 72, 2438 (1950).

$$k_h = \frac{2.303}{t\left[H_o(3+f)-B_o\right]} \log \frac{B_o(H_o-x)}{H_o\left[B_o-(3+f)x\right]}$$

where $H_o = [\text{haloform}]_o$, $B_o = [OH^-]_o$, $x = \Delta[\text{haloform}]_t$, t = time in seconds, f = fraction of the haloform going to formulate and k_h = rate constant (expressed in liters / mole of haloform x seconds).

Determination of f

It was necessary to calculate f (fraction of haloform going to formate) for dichlorofluoromethane only since reliable values for bromochlorofluoromethane were known[4]. The following relation has been derived[5]

$$3+f = \frac{\text{Base Used}}{\text{Haloform used}}$$

Therefore, a solution of dichlorofluoromethane was allowed to react with a known amount of standard base and the chloride concentration determined after all the base had been used[3]. The concentration of base was varied to see if f was dependent on base concentration.

Two 150 ml. (A,H), one 100 ml. (B), one 50 ml. (C) one 25 ml. (D) samples of 0.2809 N sodium hydroxide were

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(4) Dowell, op. cit., pp. 81 and 84.

(5) Ibid., p. 16.

pipetted separately into 250-ml. volumetric flasks and then diluted to a final volume of 250 ml. at room temperature (24^{o}). The flasks were placed in an ice bath and to each flask was added about 1 ml. of dichlorofluoromethane (syringe). In addition 15 ml. samples of 0.2809 N sodium hydroxide were added to each of three 100-ml. volumetric flasks (E, F and G), diluted to 100 ml. and the flasks were placed in an ice bath. About 0.3 ml. of dichlorofluoromethane was also syringed into each of the three flasks. The solutions (A-H) were placed in a dark desk at room temperature ($23-28^{o}$) for several days until all the base had been used as indicated by phenolphthalein. Since the reactions were allowed to go until all the base was used, the amount of base used was the amount pipetted out initially. The chloride analysis was made by the Volhard method[6].

Equations for Deuterium Exchange During Concomitant Hydrolysis

The derived equations used in the calculation of rate of deuterium exchange during concomitant hydrolysis are for the following reaction mechanism

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(6) H. H. Willard and N. H. Furman, "Elementary Quantative Analysis," 3rd. ed., D. Van Nostrand Co., New York, N. Y., 1940, p. 185.

$$CDX_3 + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CX_3^- + HOD$$

$$CHX_3 + OH^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} CX_3^- + H_2O$$

$$CX_3^- \xrightarrow{k_3} CX_2 + X^-$$

Neglect k_{-1} and treat k_{-2} as a first order constant

$$\frac{-dD}{dt} = k_1BD$$

$$\frac{-dH}{dt} = k_2BH - \frac{k_{-2}B(k_1D+k_2H)}{k_{-2}+k_3}$$

where $B = [OH^-]$, $D = [CDX_3]$ and $H = [CHX_3]$. Combining these two equations

$$\frac{dH}{dB} = \frac{k_2H}{k_1D} - \frac{k_{-2}(k_1D+k_2H)}{k_1(k_3+k_{-2})D}$$

Rearrangement, substitution and integration between limits H_o and H, D_o and D gives[a]

$$\left(\frac{D_o}{D}\right)^{1-(k_h/k_1)} = \frac{[1-(k_h/k_1)]\ (H/D)-(k_h/k_2)\ +\ 1}{[1-(k_h/k_1)]\ (H_o/D_o)-(k_h/k_2)\ +\ 1}$$

Where k_h refers to the rate of hydrolysis of protohaloform

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[a]For the derivation of this equation the author is indebted to Mr. Stanton J. Ehrenson.

only as defined on page 21. This equation was expressed as

$$b = \frac{(1-a)\left[m-(D_o/D)^{1-a}m_o\right]}{(D_o/D)^{1-a}-1} \qquad (2)$$

where $b = \frac{k_{-2}}{k_{-2}+k_3}$, $a = \frac{k_2}{k_1}(1-b)$, $m_o = \frac{H_o}{D_o}$, and $m = \frac{H}{D}$.

Measurement of exchange with k_h known would leave k_1 and k_2 as the only unknowns. The values of k_2/k_1, the kinetic isotope effect for the carbanion formation from the haloform, were determined using the following equations

$$\frac{d(B_o-B)}{dt} = \frac{k_3(k_1D+k_2H)\quad(3+f)\left[B_o-(B_o-B)\right]}{k_{-2}+k_3}$$

Since $k_h = k_2k_3/(k_{-2}+k_3)$ and allow $y = B_o-B$

$$\frac{dy}{dt} = \left[(k_1/k_2)k_hD+k_hH\right](3+f)\,(B_o-y)$$

which the hydrolysis of the deuterohaloform should follow. From the definition

$$s = \left[(k_1/k_2)\,k_hD+k_hH\right](3+f) \qquad (3)$$

it may be seen that s is approximately constant because over the range of reaction followed (6-9 per cent hydrolysis for bromochlorofluoromethane and 18-25 per cent hydrolysis

for dichlorofluoromethane), H increased while D decreased and although D decreased faster than H increased, this was largely compensated by fact that k_2 is larger than k_1. Combining the last two equations and integrating with $\underline{s}$ being treated as a constant

$$s = \frac{2.030}{t} \log \frac{B_o}{B-y} \qquad (4)$$

The approximate $\underline{s}$ value calculated for each point from equation (4) was substituted in equation (3) along with a D and the H values which were the average of D_o and D, and H_o and H. Then the average of all the values of k_1/k_2 was calculated. This average value was substituted back in equation (3) along with H_o and D_o to calculate $\underline{s_o}$ and H and D to get $\underline{s}$. A plot of s/s_o vs. y for the data obtained at 0^o for run EB with dichlorofluoromethane is given in Fig. 1.

As a second approximation $\underline{s}$ has been expressed in terms of $\underline{s_o}$ and y, where $y = (B_o-B)$

$$s = s_o(1+vy-ny^2) \qquad (5)$$

where the optimum values of $\underline{v}$ and $\underline{n}$ were chosen by the method of least squares[7]. The line in Fig. 1 is a plot

(7) W. N. Bond, "Probability and Random Errors," Edward Arnold and Co., London, 1935, p. 94.

of such an equation for the data obtained at 0° for run EB with dichlorofluoromethane. The substitution of equation (5) into (3) gives

$$\frac{dy}{dt} = s_o(1+vy-ny^2)(B_o-y)$$

which may be integrated to give

$$s_o t = C_2 \ln \frac{B_o\sqrt{1+vy-ny^2}}{B_o-y} + \frac{[(v/2)-nB_o]C_2}{C_1} \ln \frac{(v-2ny-C_1)(v+C_1)}{(v-2ny+C_1)(v-C_1)} \quad (6)$$

where $C_1 = \sqrt{v^2+4n}$ and $C_2 = \frac{1}{1+vB_o-nB_o^2}$

From equation (6) and the data on any point a value for $\underline{s_o}$ may be calculated and since

$$s_o = k_h(3+f)\left[(k_1/k_2)D_o+H_o\right] \quad (7)$$

then the ratio k_1/k_2 can be calculated. If the final average value obtained differed too much from the preliminary values used, the second approximation could be repeated.

Several $\underline{a}$ values (0.0, 0.1) were assumed and used to calculate corresponding $\underline{b}$ values from equation (2) for all values of D for each run. Using the assumed $\underline{a}$ values

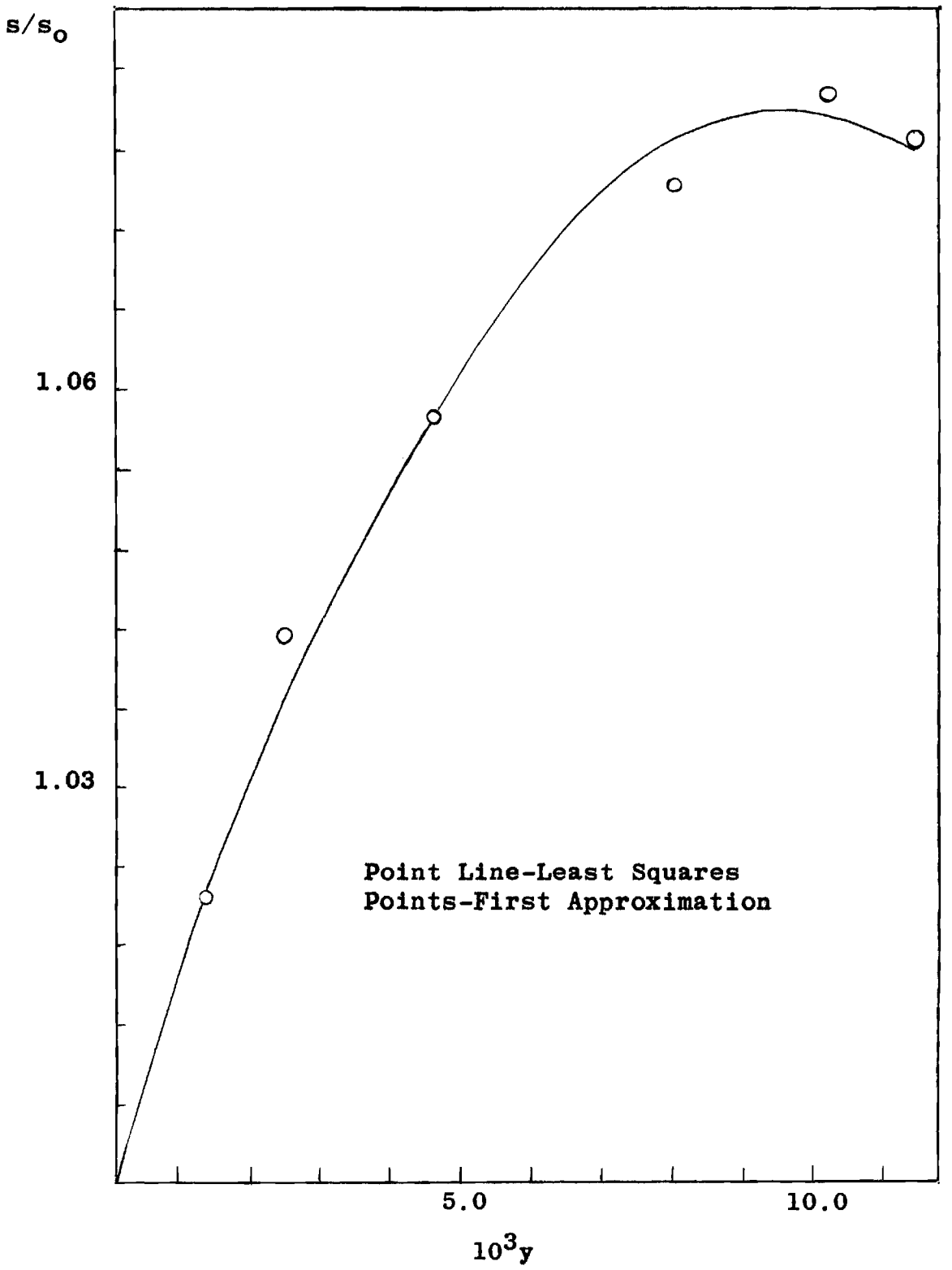

Fig. 1. s/s_o vs. y at 0^o for Dichlorofluoromethane

and their corresponding b values, a linear equation was derived using the point slope form of $b_2-b_1 = m'(a_2-a_1)$; where m' = slope of the line and a_1 was = 0. Then substituting m' in $b_1-b = m'(a_1-a)$ where b and a are unknown and solving with $a = k_2/k_1(1-b)$

$$a = - \frac{k_2/k_1(b_1-1)}{[(k_2/k_1)m'] + 1} \qquad (8)$$

with b_1 calculated from equation (2) for $a_1 = 0$. The a values from (8) were substituted in $k_1 = k_h/a$ and k_1 (rate of deuterium removal) was calculated since k_h was known. The tables in appendix 1 summarize the data for each exchange run and appendix 2 contains the derivations of the above equations.

Equation for Base-Catalyzed Deuterium Exchange with Negligible Hydrolysis

Under the conditions employed for deuterium exchange with dichloroiodomethane and dibromochloromethane, the hydroxide concentration and haloform concentration remained almost constant. Therefore, the exchange reaction for both haloforms was pseudounimolecular and the following equation was used[8]

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(8) J. Hine, R. C. Peek, Jr. and B. D. Oakes, J. Am. Chem. Soc., 76, 827 (1954).

$$k_1 [OH^-] = \frac{2.303}{t} \log \left(p+p \frac{[CHX_3]_t}{[CDX_3]_t}\right)$$

where p is the isotopic purity of the starting deuterohaloform ($p = D_o/D_o+H_o$)

The first points in all exchange runs were taken after at least ten per cent exchange had occurred and final points were taken slightly beyond fifty per cent exchange for all haloforms studied except bromochlorofluoromethane. The last point for this haloform was taken after thirty-two per cent exchange had taken place because of the small difference between the rates of hydrolysis and exchange.

General Base Catalysis

Due to the rapid rate of exchange of dibromochloromethane and dichloroiodomethane at the temperatures studied, it was necessary to decrease the hydroxide ion concentration by using an ammonium perchlorate buffer. By varying the buffer concentrations while keeping the ionic strength constant, the possibility of general base catalysis was investigated. In this case the kinetic equation takes the form[8]

$$k_1 [OH^-] + k' [NH_3] = \frac{2.303}{t} \log \left(p+p \frac{[CHX_3]_t}{[CDX_3]_t}\right) \qquad (9)$$

where k' is the rate constant for the rate of removal of deuterium by ammonia.

The hydroxide ion concentration for the buffer concentrations and ionic strength used at the temperature maintained were determined by extrapolation from the data of Everett and Wynne-Jones[9]. Since values for the right side of equation (9) were determined at two different ammonia and hydroxide ion concentrations, k_1 and k' could be determined. The values for k_1 and k' are found in the tables of appendix 1.

Heat and Entropy of Activation

The heats and entropies of activation were calculated from the absolute rate equation[10]

$$k = \frac{kT}{h} e^{-\Delta H^{\ddagger}/RT} e^{\Delta S^{\ddagger}/R}$$

Errors and Deviations

All ± values listed in the tables of appendix 1 are average deviations. Any rate constant that had a deviation which was > 2.5 times the average deviation (with it initially included) was not included in the final average.

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(9) D. H. Everett and W. F. K. Wynne-Jones, Proc. Roy. Soc. (London), A169, 190 (1938).

(10) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N.Y., 1941, p. 14.

The deviations listed for the deuterium exchange of dichlorofluoromethane and bromochlorofluoromethane were those ascribed to deviations in a values. Although the k_h values determined and used to calculate k_l ($k_l = k_h/a$) had deviations as listed, those deviations were not used.

In order to determine k_l and k' for dichloroiodomethane and dibromochloromethane, it was necessary to use the difference between two values with average deviations. The value obtained had an average deviation which was obtained by taking the square root of the sum of the squares of two average deviations[11]. The average deviations of k' were large and in some cases the average deviation was greater than the rate obtained. The k' values may be considerably in error since they were obtained from a small difference between two numbers.

Preparation and Purification of Reagents

Dichlorofluoromethane.--Matheson Chemical Co. dichlorofluoromethane (Freon 21) was distilled from concentrated sulfuric acid and used in that form.

Deuterodichlorofluoromethane.--Thirty ml. of commercial dichlorofluoromethane (Freon 21) and a 17 ml. solution of

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(11) Bond, op. cit., p. 67.

sodium deuteroxide and deuterium oxide (obtained from the D. A. Stuart Oxygen Co. on allocation from the Atomic Energy Commission) were placed in a 125-ml. erlenmeyer flask equipped with a 24/40 joint. The basic solution was prepared from 1.9 g. (0.08 mole) of sodium metal and 99.8 per cent deuterium oxide. The flask was equipped with a magnetic stirrer and a dry-ice cold finger with a calcium chloride tube connected to the side arm of the condenser and leading to a test tube in a dry-ice trap. To the erlenmeyer was added a small amount ($\sim$ 50 mg.) of solid thymolphthalein indicator and the solution was allowed to reflux for twelve hours at room temperature (approximately 28^{o}) while being agitated by the stirrer. The haloform mixture was allowed to distill and captured in the trap. The basic water solution was distilled and the "heavy" water mixture was used again to prepare a new solution of sodium deuteroxide. More 99.8 per cent deuterium oxide was added to give a final volume of 17 ml. The procedure was repeated for periods of fourteen and ten hours. With a final mixture of 10 ml. of "heavy" water from the previous three runs and 7 ml. of 99.8 per cent deuterium oxide, a new 17 ml. solution of sodium deuteroxide was prepared. This mixture and the haloform mixture from the previous three runs were mixed and allowed

to react for an additional twenty-six hours. The final mixture contained 68.15 per cent deuterodichlorofluoromethane with a final volume of about one half of the starting volume. At no time did the deep blue color of the indicator become colorless. It did become lighter on several occasions indicating that much of the base had been used.

Dichloroiodomethane.--This haloform was prepared with the procedure used by Dowell[12]. The crude product from the reaction of 350 g. of mercurie chloride (1.29 moles) with 550 g. (1.39 moles) of iodoform was fractionated through a 90-cm. Todd column to give 178.2 g. (59 per cent yield) of a light yellow liquid (b.p. 50° at 45 mm., $n^{20}D$ 1.5864, $n^{24}D$ 1.5838).

Dowell reported a b.p. of 47° at 38 mm.[12]. Diphenylamine (0.1818 g.) was added as an inhibitor and the liquid was stored under nitrogen in a brown bottle in the refrigerator.

Deuterodichloroiodomethane.--About 10 ml. of dichloroiodomethane and a solution made from approximately 34.5 per cent deuterium oxide and 2.0 g. of metallic sodium were placed in a 125-ml. low actinic erlenmeyer flask. The flask was equipped with a magnetic stirrer and a stopcock outlet. After

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(12) Dowell, op. cit., p. 19.

a small amount of solid thymolphthalein ($\sim$50 mg.) was added to the two-phase system, the flask was flushed with nitrogen and then evacuated by means of a water aspirator while the flask was immersed in ice. The stopcock was closed, the ice was removed and the system was stirred rapidly during exchange in the dark for about two and one half hours at room temperature (29°). The two-phase layer was separated in diffused light under nitrogen and the haloform was washed with 5 ml. of concentrated hydrochloric acid and then with tap water and dried over indicating silica gel. This procedure was repeated twice using sodium deuteroxide prepared from 34.5 per cent deuterium oxide and then after adding an additional 5 ml. of dichloroiodomethane, finally using 99.8 per cent deuterium oxide with the exchange going for three hours at 31°. The final volume of product was about 10 ml. of the haloform containing at least 85.1 per cent deuterodichloriodomethane, $n^{32}D$ 1.5790. The haloform was stored under nitrogen with 0.1 per cent diphenylamine in a brown bottle in a refrigerator.

Dibromochloromethane.--Dow Chemical Co. dibromochloromethane was used after fractionation through a 30-cm. tantalum spiral column 4-mm. in diameter. Approximately 15 ml. of the commercial haloform was dried over indicating silica

gel and distilled from about 2 g. of phosphorus pentoxide with a small amount of glass wool in the neck of the flask to prevent excessive frothing. The system was flushed with nitrogen and fractionated under nitrogen. The fraction with b.p. 117.0-117.6° at 737 mm. was collected and stored under nitrogen, $n^{24}D$ 1.5450; Dowell[13] reported b.p. 116.0-116.5°; $n^{25}D$ 1.5450.

Deuterodibromochloromethane.--One hundred four and six tenth grams of dibromochloroacetaldelyde (0.45 mole) and a solution prepared from 50 g. of 99.6 per cent deuterium oxide and 10.7 g. of metallic sodium were mixed in a 125-ml. round-bottomed flask that had been flushed with nitrogen. The mixture immediately turned a golden yellow and was very thick and lumpy. The meniscus between the water and organic layer was very difficult to see and it was necessary to allow the mixture to stand several minutes in order for them to separate. The two layers were separated as soon as possible to minimize hydrolysis and the organic layer was washed with 15 ml. of concentrated hydrochloric acid, then three times with 10 ml. of tap water and finally dried over silica gel. The haloform was distilled under nitrogen from approximately

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(13) Ibid., p. 21.

2 g. of phosphorous pentoxide through a small vacuum-jacketed glass-helices-packed column that was 50-cm. in length, 2-cm. in diameter and had a 2 ml. holdup. The colorless liquid fraction, b.p. 117.1-117.6° at 737 mm., was collected and stored under nitrogen. The yield was 74.1 g. (80.1 per cent) of crude and 61.0 g. (65.8 per cent) of the above fraction, $n^{34}D$ 1.5390; the haloform was at least 92.99 per cent deuterodibromochloromethane.

Dibromochloroacetaldehyde.--Essentially, the procedure of Jacobsen and Neumeister[14] was used. In a 500-ml. 3-necked round-bottomed flask equipped with stirrer, condenser and dropping funnel was placed 139.5 g. (0.91 mole) of ethyl chloroacetal. A water bath surrounded the flask while 102.4 ml. (2 moles) of bromine was added slowly over a two hour period. Gentle refluxing was noted during the addition of bromine and large quantities of hydrogen bromide were liberated. After addition of bromine, the crude liquid was gently refluxed for 15 minutes. The crude material was distilled through a Todd column at 740 mm. yielding two fractions, b.p. 147-148°, $n^{29.5}D$ 1.5362 and b.p. 148-149,

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(14) O. Jacobsen and A. Neumeister, Ber., 15, 600 (1882).

$n^{29.5}D$ 1.5290. Jacobsen and Neumeister listed b.p. 148-149. Final yield for both fractions was 130 g. (60.2 per cent).

Bromochlorofluoromethane.--The method of Singley[15] was used for the preparation of bromochlorofluoromethane. Forty eight and five tenths g. (0.23 mole) of fractionated dibromochloromethane and 25 g. (0.11 mole) of freshly opened Harshaw Technical grade mercuric fluoride were allowed to react. The crude haloform product (21.4 g.) was collected and fractionated through the vacuum-jacketed glass-helices-packed column. The fraction, b.p. 35.9-36.4° at 741 mm., was collected in a receiver surrounded by dry-ice acetone to yield 18.7 g. (54.5 per cent), $n^{26}D$ 1.4140. Dowell listed[16] b.p. 36.0-36.7°, $n^{25}D$ 1.4143.

Deuterobromochlorofluoromethane.--The procedure for the protohaloform was used. Forty-seven and two tenth (0.23 mole) of deuterodibromochloromethane and 25 g. (0.11 mole) of mercuric fluoride were used and yielded 23.4 g. of crude material. This material on fractionation yielded 18.1 g.

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(15) J. E. Singley, Jr., "Carbon Dihalides as Intermediates in the Basic Hydrolysis of Haloforms," Unpublished M. S. Thesis, Georgia Institute of Technology, 1952, p. 20.

(16) Dowell, op. cit., p. 20.

(53.7 per cent) of colorless material with b.p. 35.8-36.2 at 740 mm., $n^{28}D$ 1.4133; the haloform was at least 95.98 per cent deuterobromochlorofluoromethane.

Sodium hydroxide.--Standard sodium hydroxide solutions were prepared from a 50 per cent carbonate-free sodium hydroxide solution. A prepared 50 per cent solution was cooled to about 10^{o} and filtered by suction through a medium or coarse sintered-glass funnel under a nitrogen atmosphere. The clear solution was stored under nitrogen in a polyethylene bottle and added as needed to carbonate-free distilled water in order to prepare more dilute solutions. These solutions were standardized against standard hydrochloric acid, potassium phthalate or perchloric acid using phenolphthalein or bromothymol blue indicators.

Perchloric acid.--Baker's Analyzed Reagent grade (71 per cent) perchloric acid was diluted with carbonate-free distilled water to the approximate desired concentration and standardized against standard sodium hydroxide using phenolphthalein indicator.

Hydrochloric acid.--The general method was to use a weighed amount of constant boiling hydrochloric acid and dilute with distilled water to a given volume. The normality was checked against standard sodium hydroxide.

Ammonia-ammonium perchlorate buffer.--A technical grade of aqueous ammonia was boiled and ammonia was collected in carbonate-free distilled water under a nitrogen atmosphere. The ammonium hydroxide-ammonia solution was standardized against standard perchloric acid using 4 drops of a 1 per cent solution of methyl orange indicator. The base was pipetted by nitrogen pressure to minimize loss by volatilization. A calculated amount of standard base was pipetted into a measured amount of standard perchloric acid and the mixture was diluted to a given volume with carbonate-free distilled water. The ammonia concentration was checked against standard perchloric acid with methyl orange indicator.

A more dilute buffer was prepared by diluting a measured amount of the above buffer with carbonate-free distilled water after having added a weighed (platform balance) amount of G. Frederick Smith Co. hydrated sodium perchlorate to keep the ionic strength constant. This buffer was also checked against perchloric acid.

Sodium deuteroxide.--Sodium was cut under nitrogen, weighed on a platform balance under nitrogen and placed in a 25-ml. pyrex test tube with a side arm. The test tube contained a small piece of iron on the bottom of the tube between the sodium and the glass. Nitrogen was passed through the side

arm and "heavy" water was added slowly. When the reaction was complete, the solution was diluted to the desired volume.

For the preparation of sodium deuteroxide used in the decomposition of dibromochloroacetaldelyde, the sodium was cut in a dry box under nitrogen.

Solvents.--The isooctane and carbon disulfide were a commercial solvent grade and were used without further purification. Distillation of the carbon disulfide did not change the infrared spectrum.

Stopcock grease.--Lubriseal (A. H. Thomas Co.) grease was used in all experiments run. Spectra of this grease in both solvents used showed that it did not interfer at the bands used while Dow Corning High Vacuum grease would interfere if it were dissolved to any extent in a solvent.

Fluoroform and deuterofluoroform.--In an effort to prepare deuterofluoroform, a method was devised and tested by preparing fluoroform. Sodium trifluoroacetate was prepared by neutralizing a 20 ml. sample of trifluoroacetic acid (Minnesota Mining and Mfg. Co.) with a concentrated solution of sodium hydroxide. The solution was evaporated rapidly to dryness at approximately 140°. To a 2-l. round-bottomed flask equipped with a two hole rubber stopper and two stopcocks was added a mixture of finely powdered sodium hydroxide

(2.3 g.) and sodium trifluoroacetate (4.0 g.). One stopcock led to a pump; the second led to a closed barometer type manometer. The total volume of the system including each stopcock was 2184 ml.

The system was evacuated to about 2 mm. pressure and the flask was heated very slowly over a period of an hour to 150° as indicated by a thermometer immersed between the mantel and flask. The stopcock to the pump was closed and the temperature was slowly raised to 185-195°. The pressure would usually rise to about 40 mm. during the last temperature change. At approximately 190° the reaction mixture would fuse and then go off spontaneously. The pressure would jump to approximately 750 mm. and then fall rather rapidly as the flask was allowed to cool to give a pressure of about 350 mm. at 35°. A saturated sodium chloride solution was passed into the still partially evacuated system. By connecting an evacuated 500-ml. round-bottomed flask equipped with stopcock and wrapped with tape to the other stopcock, fluoroform was forced from the reaction flask by applying gentle pressure to the sodium chloride solution. The infrared spectrum of the gas was then determined on a Beckman IR-2 instrument and compared with the spectrum of a sample of Du Pont Commercial Fluoroform (Freon 23) and the spectrum

listed by Herzberg and Bernstein[17]. Table 26 in appendix 2 describes the spectra.

The same procedure was repeated using sodium deuteroxide and the spectrum of the deuterofluoroform was determined.

Several discrepancies between the spectrum of the prepared fluoroform and that of the commercial fluoroform showed that possible impurities were present. An attempt was made to purify the fluoroform by passing it through a series of potassium permanganate, cuprous chloride and sodium hydroxide solutions. The attempt seemed to fail.

Qualitative test for fluoride ion.--Two methods were used in an attempt to determine if fluoride ion was present in the t-amyloxide solutions. The first method[18] consisted of treating a water extract of the t-amyloxide solution with acetic acid and boiling off any t-amyl alcohol. The solution was filtered and treated with a few drops of a saturated solution of calcium chloride. After four hours no precipitate was noted but on standing for four days a brown precipi-

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(17) G. Herzberg and H. J. Bernstein, J. Chem. Phys., 16, 30 (1948).

(18) A. I. Vogel, "A Textbook of Practical Organic Chemistry," Longmans, Green and Co., New York, N.Y., 1948, p. 904.

tate was found. This was believed to be due to a brown coloration in the original solution. A known fluoride sample gave a white precipitate in one hour.

The second method[19] consisted in saturating a piece of filter paper with a mixture of 3 volumes of a 1 per cent alizarin solution and 2 volumes of a 0.04 per cent aqueous zirconium chloride solution. The paper was allowed to dry and one drop of 50 per cent glacial acetic acid and one drop of the acetic acid solution to be tested were placed on the paper. The solution had little effect on the paper. A known solution seemed to turn the paper white while the procedure called for the paper to turn yellow.

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(19) F. Snell and F. Biffen, "Commercial Methods of Analysis," McGraw-Hill Book Co., Inc., New York, N. Y., 1944. p. 108.

CHAPTER III

DISCUSSION

Hine, Dowell and Singley[1] studied the rates of hydrolysis of various haloforms in order to investigate their reaction mechanism and the effect of structure on reactivity. For the haloforms studied they found the relative reactivities to be in the order $CHBrClF \gg CHBrCl_2 > CHBr_2Cl \sim CHCl_2I > CHBr_3 > CHCl_3 \gg CHF_3$ and the probable hydrolysis mechanism to be

$$CHX_3 + OH^- \underset{}{\overset{\text{fast}}{\rightleftharpoons}} CX_3^- + H_2O$$

$$CX_3^- \xrightarrow{\text{slow}} CX_2 + X^-$$

$$CX_2 \xrightarrow[\text{fast}]{OH^-,\ H_2O} CO \text{ and } HCO_2^-$$

Several factors that were believed to play an important part in the acidity of the hydrogen atom and thus in the rate of hydrolysis were the electronegativity of the halogens, resonance stabilization of the anion and possible steric

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(1) J. Hine, A. M. Dowell, Jr. and J. E. Singley, Jr., J. Am. Chem. Soc., 78, 479 (1956).

factors.

The stability of the anion should be increased by the ability of a halogen to contain ten electrons in its outer shell. Doering and co-workers[2] have demonstrated the probability of a d-orbital resonance for the stabilization of an α-carbanion in a number of elements below the first row of eight. The subject of possible d-orbital resonance for a number of elements has been discussed by Craig and co-workers and the orbital overlap has received extensive theoretical treatment especially for overlap of 3d-orbitals with 2p-orbitals[3].

In accordance with Pauling's[4] electronegativity values, we might expect the acidity and thus the rate of removal of a proton in a haloform by the hydroxide ion to be in the order of $CHF_3 > CHCl_3 > CHBr_3 > CHI_3$. Marvel, Copley and Ginsberg[5] measured the heat of mixing per mole

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(2) W. von E. Doering and L. K. Levy, ibid., 77, 509 (1955); W. von E. Doering and K. C. Schreiber, ibid., 77, 514 (1955); W. von E. Doering and A. K. Hoffman, ibid., 77, 521 (1955).

(3) D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel and L. E. Sutton, J. Chem. Soc., 332 (1954).

(4) L. Pauling, "The Nature of The Chemical Bond," 2nd ed., Cornell University Press, Ithaca, New York, 1948, p. 64.

(5) C. S. Marvel, M. J. Copley and E. Ginsberg, J. Am. Chem. Soc., 62, 3109 (1940).

of solution of a number of haloforms with various donor solvents. Comparisons of the heats obtained when a given solvent was mixed with chloroform, bromoform or the methylene halides suggested that bromine was slightly less effective than chlorine in promoting acceptor acitivity by neighboring hydrogen atoms. Iodine was not effective to an appreciable extent. These data give a qualitative indication that the proton in chloroform should be more acidic than in bromoform as stated above. However, another factor is introduced when induction is considered and that is the inductomeric polarizability (I_d) which depends on the electronic requirements of the reaction. Thus, as the hydroxide ion attacks at the reaction center in the transition state, the negative charge of the ion will tend to repel the carbon-halogen valence electrons. Therefore, that system which tends to polarize its charges most readily will aid the removal of the proton to the greater extent. Ingold[6] lists the halogens in the order of decreasing polarizability as -I>-Br>-Cl>-F. Thus, this effect is opposite from the electronegativity

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(6) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, New York, 1953, p. 73.

effect for halogens and some indications are that the I_d effect takes precedence over the I_s effect (the permanent polarization of single bonds)[7].

Steric hindrance should be in the order of -I > -Br > -Cl > -F so as to hinder the approach of the attacking ion and also solvation by the solvent. However, formation of the carbanion would be aided in the opposite manner by B-strain[8] in that formation of the triiodocarbanion would relieve more strain than with the trifluorocarbanion.

Brockway[9] measured the bond distances of some haloforms and halomethanes and discussed their implications. The normal C-F bond length calculated from covalent bond radii is 1.41 Å and for C-Cl it is 1.76 Å[10]. On comparison of these values with experimental values it was seen that, within experimental error, the C-Cl links are of normal length in chloroform. The C-F links appear normal except in molecules containing two or more fluorine atoms, in which cases bond shortening occurs. This was explained on the basis of partial double-bond character of fluorine as in the following

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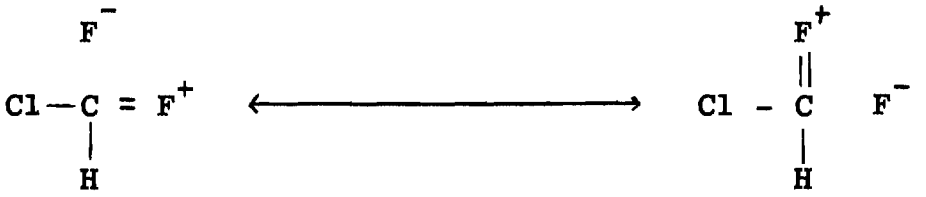
(7) E. R. Alexander, "Principles of Ionic Organic Reactions," John Wiley and Sonc, Inc., New York, N. Y., 1950, p. 11.

(8) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p. 79.

resonance structures



The normal value for C-F was observed in $CHCl_2F$ with a slight shortening indicated for the C-Cl bond. However, with $CHClF_2$, Pauling[11] believes that the C-F bond achieves about ten per cent double-bond character with the simultaneous assumption of ionic character by the other bond. The F^- $C{=}Cl^+$ interaction was believed to decrease the C-Cl bond a distance which corresponds to about five per cent double-bond character.

Since hydrolysis of a haloform has a rather complex mechanism, the measurement of proton removal from a haloform should give us a simpler idea about the effect of halogens on a structure than would hydrolysis rate studies. An attempt was made to correlate the data acquired for the rates of deuterium removal from four haloforms ($CDCl_2F$, $CDCl_2I$,

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(9) L. O. Brockway, J. Phys., Chem., 4, 185 (1937).

(10) Pauling, op. cit., p. 164.

(11) Ibid., p. 236.

$CDBr_2Cl$ and CDBrClF) along with the other existing data on exchange rates in a basic aqueous solution. Table 4 shows these rates along with their $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ values calculated in the approximate range of 0-35°.

Table 4. Rates for Base-catalyzed Deuterium Exchange of Haloforms at 0°.

Haloform	$k_1 \times 10^4$ at 0°	$\Delta H^{\ddagger}$ (kcal.)	$\Delta S^{\ddagger}$ (e.u.)
$CDCl_2F$	0.89	25.9 ± 0.6	17.7 ± 2.3
CDBrClF	21.0	24.3 ± 0.5	18.4 ± 1.7
$CDCl_3$[a]	47.0	23.5 ± 0.5	17.1 ± 3
$CDBr_2F$[b]	207		
$CDCl_2I$	275.0	22.1 ± 0.2	15.3 ± 0.5
$CDBrCl_2$[c]	290		
$CDBr_2Cl$	1435	21.3 ± 0.2	15.6 ± 0.6
$CDBr_3$[d]	5800	20.3 ± 0.5	15.0 ± 3
CDI_3[b]	6010	20.2 ± 0.8	14.5 ± 3

[a]J. Hine, R. C. Peek, Jr., and B. D. Oakes, J. Am. Chem. Soc., 76, 827 (1954).

[b]J. Hine and P. B. Langford, unpublished data.

[c]R. C. Peek, Jr., unpublished data on one point.

[d]J. Hine and M. Hine, unpublished data.

The data in the table indicates that the order of over-all halogen effect is I ~Br > Cl > F. If I were greater than Br, this is the order that might be expected for the I_d effect and B-strain and the reverse order that would be expected for the I_s effect alone.

Pearson and Dillon[12] have summarized much of the existent data on the removal of carbon-bound hydrogen by the base water. In their data a number of "anomolies" (departures from linear free energy relationships) were seen when K_a (equilibrium constants) were examined or when K_a and k_2 (rate constants for proton removal) were compared. Possibly an attempt to explain these irregularities should include a comparison of the rates of removal of α-protons by hydroxide ion with rate constants for the formation of the same carbanions by the unimolecular decarboxylation of acid anions in the same solvents. Pedersen[13] has given good evidence for a carbanion intermediate in the decarboxylation of several nitroacetate derivatives and it seems reasonable that a number of other acid anions decarboxylate through a carbanion intermediate[14].

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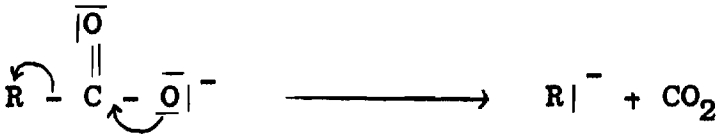
(12) R. G. Pearson and R. L. Dillon, J. Am. Chem. Soc., 75, 2439 (1953).

(13) K. J. Pedersen, J. Phys. Chem., 38, 559 (1934).

(14) Hine, op. cit., p. 283.



Haloforms appear to be well suited for the study of carbanion formations since such interfering factors as steric inhibition of resonance, internal rotation, hydration etc. are minimized. Therefore, it should be easier to ascertain the relative importance of the electronic and simple steric factors.

Table 5. Rates of Carbanion Formation.

R-H	Rate of Proton Removal (k_2 in sec^{-1} at 0^o)	Ref.	RCO_2^- Decomposition (k_d at 70^o in sec^{-1})	Ref.
$CHCl_3$	8.23×10^{-3}[a]		1.7×10^{-5}	18
$CHBr_3$	1.02[a]		9.4×10^{-4}[e]	19, 20
$CHBr_2Cl$	2.51×10^{-1}[a]		3.0×10^{-4}	21
CHBrClF	3.65×10^{-3}		2.5×10^{-6}[f]	21
CH_3NO_2	1.32[b]	15	2.0×10^{-1}[g]	13
$CH(CH_3)_2NO_2$	3.47×10^{-2}	15	3.8×10^{-2}[g]	13
$(CH_3)_2CO$	11.31×10^{-3}[c]	16	2.1×10^{-7}	22
CH_3CO_2H	1.2×10^{-6}[d]	17	1.6×10^{-7}[h]	19

[a]Assumed isotope effect of 1.75 (avg. for $CDCl_2F$ and CDBrClF)

[b]Divided literature value by statistical factor of 3 to get the rate constant per hydrogen atom.

[c]Divided literature value by statistical factor of 6.

[d]Extrapolated from 77° for exchange of one deuterium atom of CD_3CO_2H with 1N OH^- and assumed isotope effect of 1.75 as calculated for haloforms.

[e]Rate constant at 70° (5.4×10^{-4}) attributed to Fairclough by Sutherland and Aston appeared to be in error. A value of 7.1×10^{-4} sec^{-1} $mole^{-1}$ l. was the average value calculated from rate at 64.9° and 76.4° with E = 24.1 kcal. Johnson and Moelwyn-Hughes[20] obtained the constant 8.2×10^{-4} for decarboylation of tribromoacetic acid but the acid was apparently not completely dissociated because a value of 11.6×10^{-4} was obtained by an extrapolation (5.1°) of their data on the salt. A final value of 9.4×10^{-4} (average of 7.1 and 11.6×10^{-4}) was used.

[f]Calculated from Sutherland and Aston's data for excess alkali.

[g]In acetate buffer extrapolated from 17.8°.

[h]For sodium hydrogen malonate.

(15) S. H. Maron and V. K. La Mer, J. Am. Chem. Soc., 60, 2594 (1938).

(16) R. P. Bell, J. Chem. Soc., 636 (1946).

(17) K. H. Geib and L. D. C. Bok, Z. phys. Chem., A183, 353 (1939).

(18) F. R. Verhoek, J. Am. Chem. Soc., 56, 571 (1934).

(19) R. A. Fairclough, J. Chem. Soc., 1186 (1938).

Data on the decarboxylation in water for only four trihaloacetate ions were available. However, the rate constants for proton removal and decarboxylation of the corresponding acid anions for four other non-halogen compounds were available. A comparison of the rates of carbanion formation by two different routes is reported in Table 5.

A plot of log k_2 (rate of proton exchange in water at 0° with OH^-) vs. log k_d (rate of unimolecular decarboxylation of acid anion at 70° in water) was made (Fig. 2) to see if there was a correlation between the rates of carbanion formation by the two different routes. A straight line has been fitted to six of the eight points plotted. Although Fairclough[19] believed that decomposition of sodium hydrogen malonate was not going through the same mechanism as the decomposition of the other acetate anions studied, the data seemed to fit the plot fairly well. The two points for the nitro compounds do not show any correlation but this might be partially attributed to a steric factor. Although the

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(20) P. Johnson and E. A. Moelwyn-Hughes, Proc. Roy. Soc. (London), A175, 118 (1940).

(21) L. H. Sutherland and J. G. Aston, J. Am. Chem. Soc., 61, 241 (1939).

(22) K. J. Pedersen, ibid., 58, 240 (1936).

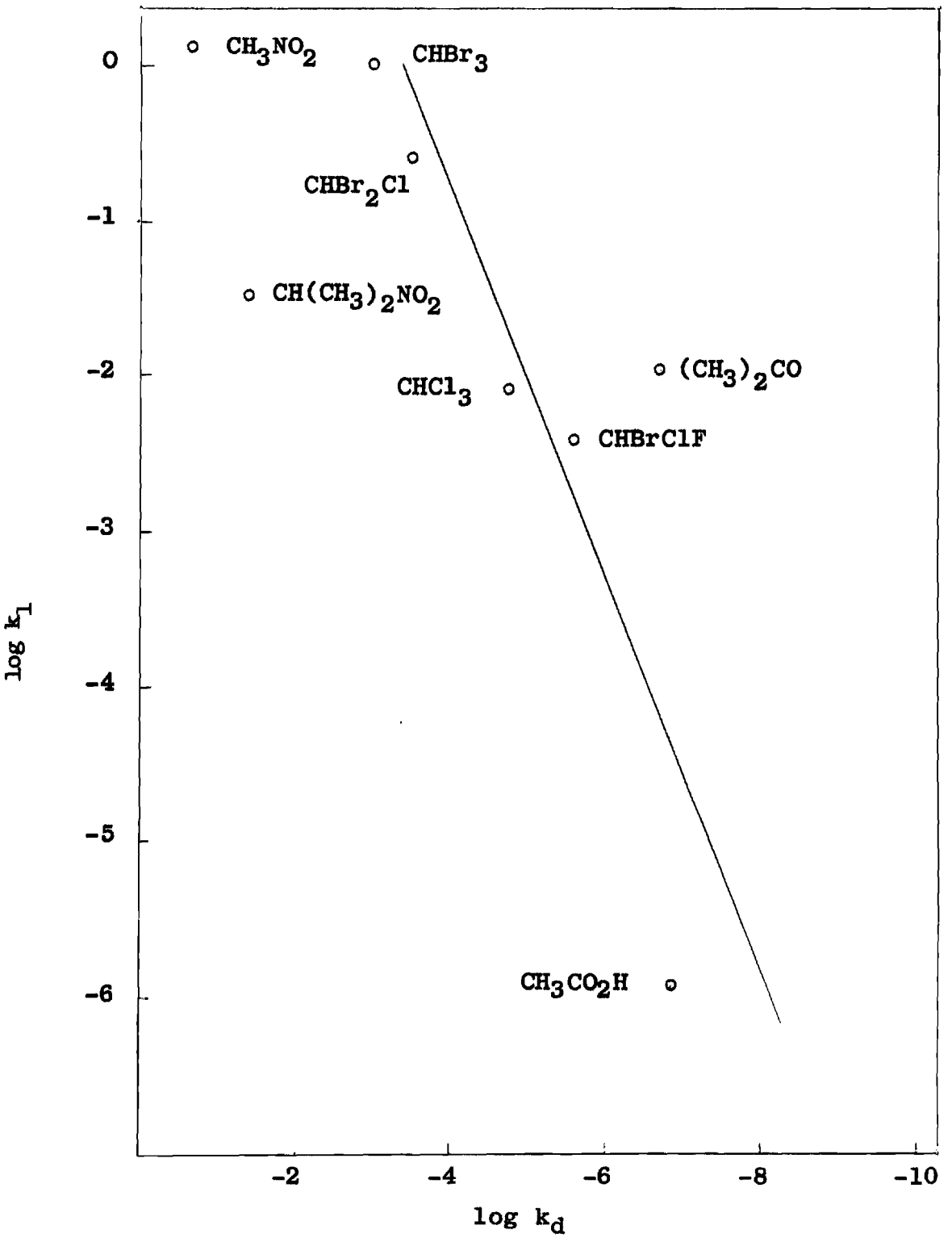
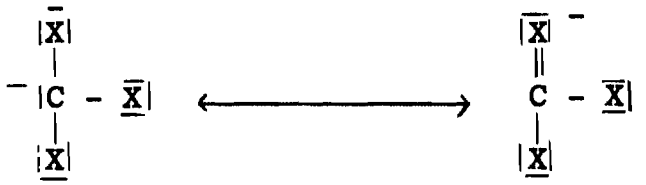


Fig. 2. Relationship Between Rates of Carbanion Formation by Two Separate Routes

rate of exchange for nitromethane is approximately 40 times as fast as that for 2-nitropropane, the rates of decarboxylation of their acid anions are about the same. This might be due to steric interaction between nitro group and the carboxy group in the acid which is alleviated to some extent when the carboxyl group is substituted by the smaller hydrogen atom.

That the resonance stabilization of a carbanion seems to be a definite driving force in aiding the removal of a proton may be inferred from the data of Bonhoeffer and coworkers[23]. The rate constant for proton removal for nitromethane is much greater than for fluoroform. It does not seem probable that this should be attributed to a greater I_s effect for a nitro group in comparison to three fluorine atoms. For resonance to stabilize a trihalomethylcarbanion (or the transition state leading to one) it seems necessary that a halogen atom must assume ten electrons in its outer shell to give the following structures



(23) K. F. Bonhoeffer, K. H. Geib and O. Reitz, J. Chem. Phys., 7, 664 (1939).

where the X's may be the same or different halogens. If this is the case, the resonance and I_s factors might be expected to show an inverse order to each other in the halogen family since fluorine is the most electronegative of the halogens but should have the greatest difficulty in making use of its d-orbital.

The effect that changing the nature of the haloform's halogen atom has on the deuterium exchange reactivity data suggested that a linear free energy relationship might exist. Table 6 shows a group of four basic mono-halogen haloforms developed by varying two of the three halogen atoms and using log $k_1 \times 10^4$ at 0^o.

Table 6. Haloform Series

XY	Cl-Cl	Br-Br	Cl-F	Cl-Br	Cl-I	Br-F	I-I
CDFXY	-0.0500	2.3160		1.3214			
CDClXY	1.6721	3.1569	-0.0500	2.4624	2.4392	1.3214	
CDBrXY	2.4624	3.7634	1.3214	3.1569		2.3160	
CDIXY	2.4392						3.7404

Several of the series were plotted against each other in Fig. 3. Three curved lines were obtained. It is not quite certain to what the type of curve obtained may be attributed but the carbanion formation might be dis-

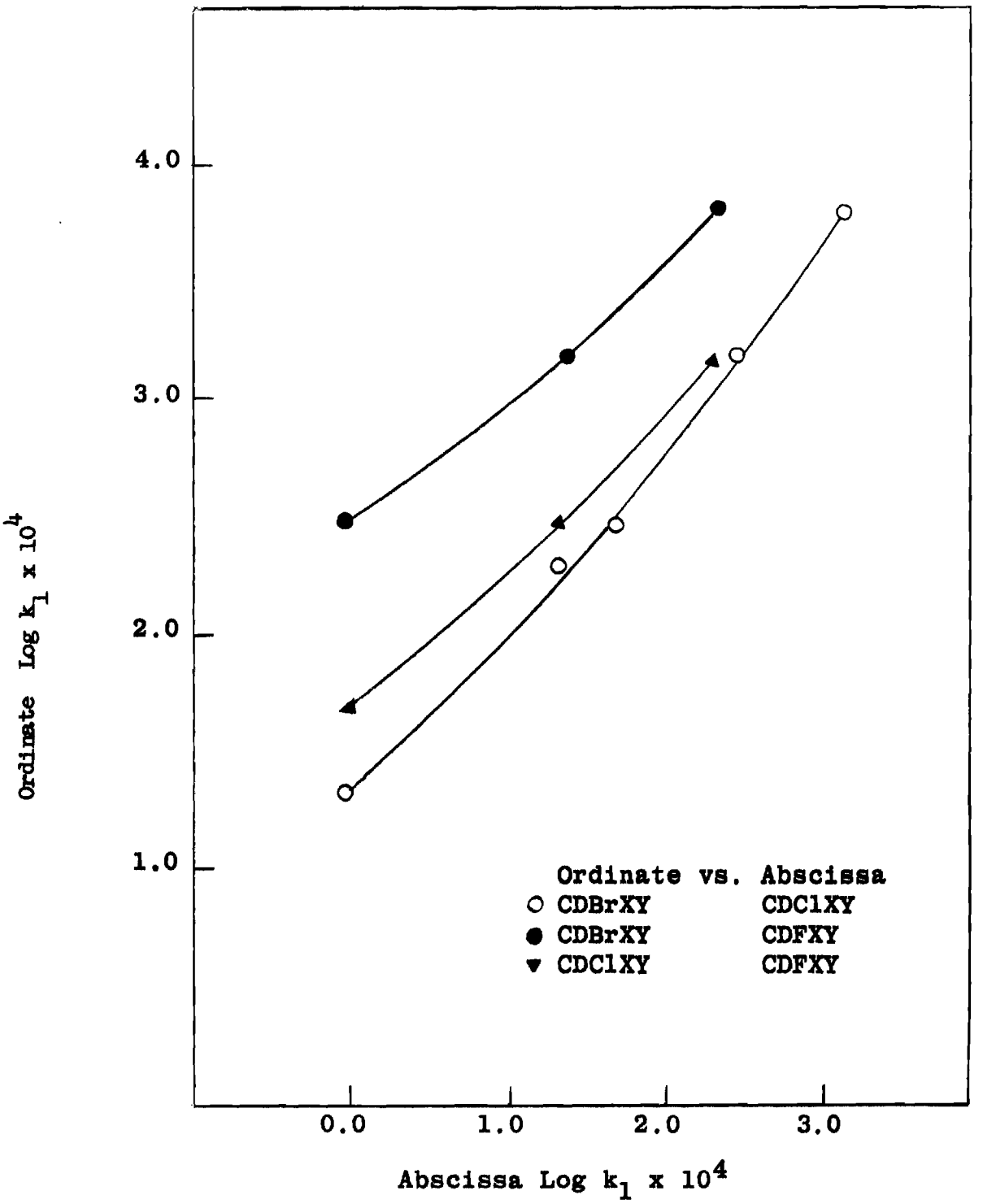


Fig. 3 Relationship Between Effects of Halogens on the Rate of Deuterium Removal

cussed briefly from the chemical kinetic viewpoint.

If for a series of reactions the $\Delta S^{\neq}$ values are found to be zero or are approximately constant, the differences in rate can probably be attributed to electronic effects for the different groups present. A difference of $\Delta H^{\neq}$ values then can be attributed to the electronic requirements of the reaction and how they are met by the groups present[24]. The formation of the transition state depends on two factors ($\Delta H^{\neq}$ and $\Delta S^{\neq}$).

It can be seen that $\Delta S^{\neq}$ values for the rate of deuterium removal are within the combined average deviation of each other. It can be noted however, that the $\Delta S^{\neq}$ values tend to fall off with increasing molecular weight and also possibly with the increasing ability to stabilize a carbanion. In order to correlate the data, it has been assumed that $\Delta S^{\neq}$ is relatively constant for the deuterium atom removal in the reaction listed. It is also assumed that the reaction intermediate or transition state for the formation of a carbanion is of the same nature in all cases studied. With this in mind it can be hypothesized that the observed rate differences in deuterium removal were due to potential-energy differences

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(24) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 184-207.

which are related to such effects as resonance and electronegativity. It had been thought that the rates found for the haloforms might be proportional to these properties. Therefore, a plot of the log of the rates of one series against another should give a straight line if a proportionality was in effect.

Leffler[25] has recently discussed a linear relationship between $\Delta H^{\neq}$ and $\Delta S^{\neq}$ for various reaction series in terms of the linear equation

$$\Delta H^{\neq} = \Delta H_o^{\neq} + \beta \Delta S^{\neq} \quad \text{(isokinetic relationship)}$$

where $\Delta H_o^{\neq}$ is the value of $\Delta H^{\neq}$ corresponding to $\Delta S^{\neq} = 0$ and β (isokinetic equilibrium temperature) is the slope of the relationship having dimensions of absolute temperature. The heats and entropies of activation listed in table 4. follow this relationship fairly well with a correlation coefficient, r, being 0.903. A least squares treatment gave an isokinetic temperature, $\beta = 1313^{\circ}K$ and $\Delta H_o^{\neq} = 1.20$ kcal./mol.

The fact that the $\Delta S^{\neq}$ values appear high, although within the experimental error, for both of the monofluorocompounds for which $\Delta S^{\neq}$ are available, might be attributed

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(25) J. E. Leffler, J. Org. Chem. 20, 1202 (1955).

to the fact that there is a slight change in the type of transition state. Also, these two compounds along with dibromofluoromethane are the only ones whose deuterium exchange was accompanied by any appreciable hydrolysis. Since fluorine appears not to stabilize a carbanion intermediate as well as the other halogens, it might be considered that the transition state could be the result of a concerted attack. In this attack the hydroxide ion might be expected to remove a hydrogen ion with a certain degree of the halogen ion being eliminated as compared to the primary hydrogen ion removal only for a carbanion formation. In terms of resonance the stability of the carbon dihalide intermediates was found to be on the order of F $>$ -Cl $>$ -Br $>$ -I. Although this was not expected, fluorine is believed to form a double bond more readily than the other halogens by electron contributions to carbon[26, 27]. Resonance stabilization might be expected from the following contributing structures[28]

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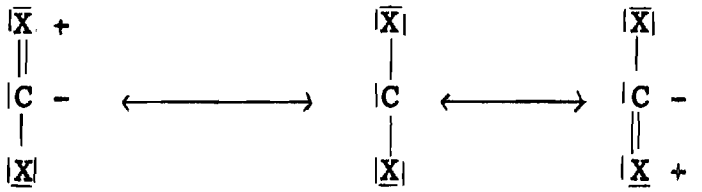
(26) Ingold, op. cit., p. 77.

(27) A. E. Remick, "Electronic Interpretations of Organic Chemistry," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1949, p. 60.

(28) J. Hine, J. Am. Chem. Soc., 72, 2438 (1950).

(29) J. Hine and D. E. Lee, ibid., 73, 22, (1951); 74, 3182 (1952).



This, however, brings in an anomaly. Hine and Lee[29] studied the effects of several α-halogens in the study of hydrolysis rates of benzotrihalides. The replacement of the first halogen atom seemed to be the rate-controlling step and the relative reactivities depended on the stability of the carbonium ion ($C_6H_5CX_2^+$). Studies indicated that an α-chlorine stabilized the intermediate carbonium ion by greater ease of double-bond formation than did bromine. However, indications were that α-fluorine was less capable of stabilizing a carbonium ion than chlorine.

If the carbon dihalide is stabilized to the greatest degree in the halogen family by fluorine, then it could be expected that with difluorohaloforms the rate of hydrolysis would approach the rate of proton removal and in fact a preliminary investigation of deuterobromodifluoromethane has indicated that they are equal[30]. The possible greater stability of a carbon difluoride intermediate in relation to a difluorocarbanion could be the important factor for the

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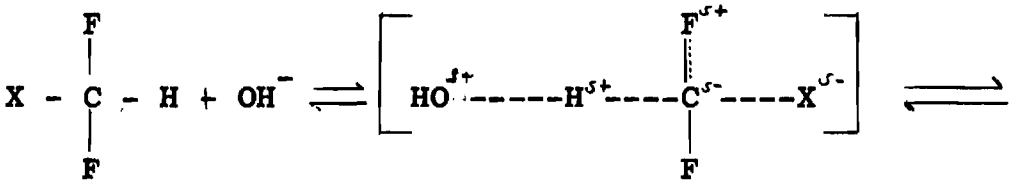
(30) J. Hine, unpublished data.

concerted attack and therefore for concomitant hydrolysis and proton removal. A critical ratio according to the stabilities of intermediates might be in effect. All haloforms may be potentially able to go by a concerted attack but the ratio of the extent of cleavage of the C-H bond to the extent of simultaneous cleavage of the C-X bond indicates to what extent we have a concerted attack. The greater the ratio of resonance stabilization for the carbon dihalide in relation to the trihalocarbanion might then be considered the determining factor. A concerted attack might take place such that a simultaneous pulling off of a proton and expulsion of a halide would occur.



CF_2 ——etc.——→

The susceptibleness of the carbon-halogen bond to being broken should be of the order $-I \sim -Br > -Cl > -F$. The fact that sodium trifluoroacetate decarboxylated (although rather reluctantly) to yield fluoroform suggests that a carbanion intermediate is involved[31]. Since the trifluoro-

carbanion would not be expected to be stabilized by resonance, this indicates that a concerted attack might also depend on the ease with which the C-X bond is broken or the X^- ion "squeezed" out by resonance stabilization in the carbon dihalide.

Attempts at decarboxylation of sodium chlorodifluoroacetate were reported[31]. Inconclusive results were obtained, but both halide ions and acid were formed.

Attempts at decarboxylation of sodium dichlorofluoroacetate below 100^o showed 23 per cent base produced indicating not only that decarboxylation had taken place but also hydrolysis ($CX_3^- + H_2O \rightleftharpoons CHX_3 + OH^-$) had taken place[31]. This could indicate that a more stable carbanion was formed from the dichlorofluoroacetate anion while the chlorodifluoroacetate was either decarboxylating without formation of an anion or was susceptible to another mechanism of breaking down other than the initial loss of carbon dioxide to form a carbanion. This does fit in with the findings of this study that dichlorofluoromethane forms a carbanion.

The rate of removal of a proton from fluoroform can

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(31) I. Auerbach, F. H. Verhoek and A. L. Henne, J. Am. Chem. Soc., 72, 299 (1950).

be predicted by checking the point of intersection on the haloform line in Fig. 2 (after extrapolation) with the known rate of decarboxylation for the trifluoroacetate anion. However, the decarboxylation was measured in ethylene glycol because of the high temperature necessary for decomposition[31]. Using the rate constant at 170° and the observed activation energy of 42 kcal., a value of $\sim 2.7 \times 10^{-11}$ sec^{-1} was obtained for the trifluoroacetate anion in ethylene glycol at 70°. This value corresponds to a rate constant of $\sim 3 \times 10^{-11}$ for proton removal for fluoroform at 0° in water using Fig. 2 and assuming that the rate of decomposition for the acetate anion was about the same in water as in glycol, as it has been found to be for the trichloroacetate anion at 76.7° (although the activation energy is lower by 5 kcal. in glycol).

It is interesting to note that Doering and Hoffman[2] stated that the contribution of d-orbital resonance remained roughly constant throughout for all elements studied below the first period of eight. For both groups of elements studied, after the first row of eight, the rates of exchange decreased on going down the periodic table. This was attributed to the effect of increasing bond length in decreasing the coulombic lowering of the activation energy. For a group of elements their method of calculating d-orbital

resonance (R_d) indicated no d-orbital resonance for the first element with the second and fourth elements contributing slightly more than the third. In conclusion it was declared that the latter three elements contribute equally. However, the fact that iodine is the only halogen to form a heptahalide (IF_7) might lead one to believe that iodine can use its d-orbits more readily than bromine or chlorine.

In a discussion of the four factors believed to affect the rate of removal of a proton, it is believed that no one specific effect can be quantitatively determined from the data. The largest increases in rates seem to be attributed to resonance and I_d effects. If fluoroform's extrapolated rate constant of $\sim 10^{-11}$ is used, it is found that chloroform has a rate that is $\sim 10^8$ times greater. This increase should be attributed to d-orbital resonance, I_d effect and B-strain (steric factor) since I_s effect would be expected to be stronger for fluoroform. If it is assumed that fluorine has no d-orbital resonance, then it might be postulated that the largest single factor is resonance. This seems reasonable since iodoform's rate is only $\sim 10^3$ times that for chloroform and in both cases resonance stabilization should be in effect.

If the data in table 4 are examined, it appears that

the rate of deuterium removal for deuteroidoform is equal to or greater than the rate for deuterobromoform. Steric effects usually increase rather sharply with increasing size once they occur. These effects should be largest with iodoform and if we compare deuteroiodoform with deuterobromoform, this help should show to a larger extent than if we compare deuterobromodichloromethane with deuterodichloroiodomethane. The data show that the effect of iodine compared to bromine is small and in fact within experimental error. At most a steric effect of no more than about ten per cent can be assumed: with the other haloforms this effect should be smaller.

Tiers[32] has recently given the following evaluations of apparent electron-withdrawing power as judged by nuclear spin resonance values for the F atoms of the CF_2 group in perfluoralkyl chlorides, bromides and iodides: I > Br > Cl > F. This order indicates the decreasing order of shielding of the fluorine nucleus by its electron cloud (showing greater electron withdrawing power than indicated by the standard perfluoro group). This worker felt that the bulkiness of substituents such as I has the effect of compensating for

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(32) G. V. D. Tiers, ibid., 78, 2914 (1956).

their lesser electronegativity in producing "electron withdrawal" from a nearby group (CF_2). This observation might indicate that in the case of haloforms, there is no steric factor with I and Br but an "apparent electron-withdrawal" (repulsive interactions with neighboring groups in the molecule).

An I_s effect can be shown by comparing the rate constants for deuterobromodichloromethane and deuterodichloroiodomethane. Although the difference is small, we find that the first haloform has a slightly larger rate constant. Any difference due to I_d, B-strain or d-orbital resonance effects should favor dichloroiodomethane. Therefore, it might be assumed that this small increase is due to an I_s effect.

A comparison of the rates of proton removal for nitromethane and chloroform showed that nitromethane reacts $\sim 10^2$ times faster. If the steric effects are discounted, the difference in rates for nitromethane and chloroform seem to be the result of resonance and I_d effect since the I_s effect should vary in the opposite direction (trichloroacetic acid is stronger than nitroacetic acid). Examination of specific refraction constants (atomic refractive)[33] suggests that the

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(33) N. Lange, "Lange's Handbook of Chemistry," 6th ed., Handbook Publishing Co., Sandusky, Ohio, p. 1025.

I_d effects should be larger for chloroform. Therefore, the difference in rates seems to stem from a greater resonance stabilization in nitromethane by the nitro group. The fact that bromoform and iodoform have rate constants that are over 10^3 greater than chloroform certainly indicates either a larger d-orbital or I_d effect or both. If the statement of Doering and Hoffman[2] that the d-orbital resonance is approximately constant past the first row of eight is accepted, the influence of bromine and iodine on the reactivity must be attributed to the I_d effect (acting with the I_s effect). However, Doering and Hoffman did not consider the I_d effect. If they had have, they might have postulated a different order of facility for d-orbital resonance. Since the largest difference in specific refraction constants for the halogens (almost a six-fold difference) occurs between fluorine and chlorine, perhaps much of our observed data could be explained on the basis of the I_s effect and I_d effects rather than the I_s effect and d-orbital resonance. It is not clear how a definite experimental distinction between the I_d effect and d-orbital resonance could be made.

It has been found that d-orbital resonance, the I_d effect or both increased the rate of proton removal by the largest factors for the haloforms. This does not,however,

necessarily mean that they are the most important effects. The I_S factor could very well be the determining factor as to whether proton removal will actually take place. A point of saturation may be almost reached by placing three halogens on the same carbon atom. Further substitution of any one of the halogens by a more electronegative halogen may show only a very small effect on the rate, thus indicating a lesser importance for the I_S effect.

It was mentioned earlier that hydration is probably minimized. A more accurate statement would be that it is hoped that hydration is minimized. Hydration has been found to take place in a number of haloforms and a very good example of this was shown with dichlorofluoromethane. Banks, Heston and Blankenship[34] have described the formation of a crystalline haloform hydrate that forms in water at 0°. This could indicate a possible orientation of a cloud of water molecules surrounding and interacting with a haloform. It can not be said to what extent one might expect this effect to operate on proton removal. It does not, however, seem probable that this factor will be constant for all the haloforms studied. In fact it might seem that this factor would have a tendency

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(34) W. P. Banks, B. O. Heston and F. F. Blankenship, J. Phys. Chem., 58, 962 (1954).

to be more profound with the haloform with the largest I_s effect and thus cause a possible shielding of the molecules from the hydroxyl ion. Thus the I_s effect could be leveled to some extent due to the presence in a molecule of three strongly electronegative halogens.

Salt effects should be negligible at the concentrations used during exchange[35].

The kinetic isotope effect has been measured for bromochlorofluoromethane and dichlorofluoromethane and the assumption was made that it would be about the same for dichloroiodomethane and dibromochloromethane. The values of k_1/k_2 (the kinetic isotope effect for carbanion formation from the haloform) increases with increasing temperature as would be expected from theoretical considerations[36]. The data suggest that the hydrogen being transferred in the reaction is held rather tightly in the transition state.

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(35) See ref. a in table 4.

(36) K. B. Wiberg, Chem. Revs., 55, 713 (1955).

CHAPTER IV

CONCLUSIONS AND RECOMMENDATIONS

The rate constants for deuterium removal in basic aqueous solution by hydroxide ion were measured for dichlorofluoromethane, dichloroiodomethane, dibromochloromethane and bromochlorofluoromethane. The two fluorohaloforms showed concomitant hydrolysis during exchange while the other two haloforms were found to be pseudounimolecular in reaction. It was believed that general base catalysis was demonstrated but the values reported were obtained from a small difference between two large numbers.

The rate constants for deuterium removal in basic aqueous solutions were available for five other haloforms. When these data were incorporated with the data for the above four haloforms at 0°, they were found to be in the order $CDI_3 \sim CDBr_3 > CDBr_2Cl > CDBrCl_2 \sim CDCl_2I > CDBr_2F > CDCl_3 > CDBrClF > CDCl_2F$. This general order differs considerably from the order obtained for hydrolysis[1]. The over-all halogen effect was $I \sim Br > Cl > F$ for carbanion formation.

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(1) J. Hine, A. M. Dowell, Jr. and J. E. Singley, Jr., J. Am. Chem. Soc., 78, 479 (1956).

All indications were that B-strain (steric factor) was a small (10 per cent or less) contributing factor to the rate of deuterium and protium ion removal. The inductive (I_s), inductomeric polarizability (I_d) and d-orbital resonance effects were found to be intangible from a quantitative standpoint in light of the available data. The largest changes in rate constants could be attributed to d-orbital resonance and the I_d effects. It was questionable whether d-orbital resonance was a reality or if the differences in the rate constants might be due only to the I_d effect since any effect that might be attributed to d-orbital resonance could be also explained by the I_d effect alone. It could not be determined which one of the latter three effects was the most important for proton removal. Although the I_s effect seemed to be the smallest of the latter three effects, no evidence was present to indicate its actual importance in deuterium or protium ion removal.

Since concomitant hydrolysis during exchange had been found to increase in haloforms containing a fluorine atom, it was believed that the transition state during exchange for these haloforms would be somewhat different from the transition for the non-fluorohaloforms. Possibly a concerted attack on the fluorohaloforms might take place

as compared to the primary proton removal for the other non-fluorine compounds.

A comparison of the rates of carbanion formation by two different routes for four haloforms and four other compounds was made. A straight line relationship was shown for six of the eight compounds. A relationship between the effects of halogens on the rate of deuterium removal was also attempted. Three non-parallel curves were obtained. These plots can be used to predict the rate constants for deuterium removal for other haloforms whose rates have not as yet been determined.

Further exchange studies should be made with difluoro-haloforms such as deuterodifluorochloromethane and deutero-difluoroiodomethane. If the expected rate values appear out of line or the $\Delta S^{\ddagger}$ values calculated are not in the range of $\Delta S^{\ddagger}$ values for the other haloforms, it might be correct to assume that a different transition state is involved for the difluorohaloforms. A change in the isotope effect value compared with the monofluorohaloforms might also be expected if a concerted attack takes place. This might be so especially with the above mentioned difluorohaloforms since the rate of removal of the deuterium or protium ion in a concerted attack should be dependent to some extent upon the ease

of elimination of the halide ion while the system is forming the carbon dihalide intermediate. The isotope effect for these compounds might possibly show a large enough difference with the monofluorohaloforms to indicate a change of mechanism.

APPENDIX 1

Review of Some Symbols Used in Following Tables.

Basic hydrolysis

Δ ml. $\underline{N}$ OH^-	ml. of standard base (see page footnotes for normality) used during reaction
$\Delta [OH^-]$	molar concentration of base used during reaction
	$[OH^-]_o - \Delta [OH^-] = [OH]_t$
f	$[OH^-]_o / 2 [Cl^-]$

Deuterium exchange with hydrolysis

m_o	H_o/D_o
m	H/D
m'	slope of line obtained; m' = $\frac{b_2-b_1}{a_2-a_1}$ where $a_1 = 0$
b_1	value obtained for $a_1 = 0$
a	$\frac{k_h}{k_l}$

General

*	indicates values which are felt to be representative of all data

Table 7. Basic Hydrolysis of Dichlorofluoromethane in Water at 0°.

Run A. and C.

No.	t(sec.)	$[CHCl_2F]_o$	Δml. N OH^-	$\Delta[OH^-]$	$10^5 k_h$ liter/mole x sec.
3	206117	0.0293	2.46	0.00762	1.306[a]
4	271890	.0357	3.43	.01062	1.216
5	301337	.0315	3.42	.01059	1.248
6	307910	.0341	3.70	.01146	1.244
8	347730	.0352	4.09	.01266	1.230
9	428240	.0309	4.33	.01341	1.233
					Av. 1.234 ± 0.010*

No.	t(sec.)	$[CHCl_2F]_o$	Δml. N OH^-	$\Delta[OH^-]$	$10^5 k_h$ liter/mole x sec.
1	262680	0.0288	2.850	0.00485	1.221
2	500740	.0206	3.138	.00534	1.021[a]
3	586470	.0291	5.038	.00857	1.155
5	686220	.0285	5.518	.00938	1.160
6	774000	.0310	6.168	.01049	1.138
					Av. 1.169 ± 0.027

[a]Not averaged (> 2.5 average deviation). f = 0.72

$[OH^-]_o$ = 0.03096 M for run A and 0.01700 M for run C. Stopped reactions with 4.00 ml. of 1.190 N $HClO_4$; blank for run A was 5.36 ml. of 0.3096 N NaOH. Stopped No. 1 of run C with 15 ml. of 0.1090 N HCl and Nos. 2-6 with 10 ml. of 0.2229 N $HClO_4$; blank for run C was -0.48 ml. for No. 1 and 3.112 ml. for Nos. 2-6 of 0.1700 N NaOH.

Table 8. Base-catalyzed Deuterium Exchange of Dichlorofluoromethane in Water at 0°

Run EB.

$[OH^-]_o$ = 0.0170 M $D_o/(H_o + D_o)$ = 0.6310

m_o = 0.5848

No.	t(sec.)	H_o+D_o	$\Delta[OH^-]$	H+D	D/(H+D)	m	m'
2	77060	0.03157	0.00135	0.0312	0.5728	0.7459	0.6560
3	170325	.03039	.00249	.0297	.5177	.9316	.7470
5	258830	.03458	.00455	.0334	.4591	1.1780	.8555
6	521660	.03555	.00816	.0334	.3737	1.6762	1.0351
7	838160	.03127	.01021	.0285	.3038	2.2917	1.2315
8	947715	.03345	.01142	.0304	.3003	2.3302	1.2040

$s = s_o(1+16.7y-870.5y^2)$

No.	b_1	s/s_o[b]	s/s_o[c]	k_1/k_2	a	10^5k_1
2	0.8234	1.0211	1.0201	0.5728	0.1449	8.516
3	.8226	1.0406	1.0364	.4523[e]	.1354	9.114
5	.8119	1.0573	1.0580	.5796	.1331	9.271
6	.7799	1.0748	1.0783	.5724	.1377	8.962
7	.7519	1.0810	1.0798	.5564	.1381	8.936
8	.7515	1.0780	1.0774	.5566	.1402	8.802
				Av. 0.5676[d] ± .0088		

[b]First approximation - see figure 1 plot of b and c vs. $\Delta[OH^-]$

[c]Method of least squares

[d]0.5832 by first approximation

[e]Not averaged (> 2.5 average deviation);

k_1 = 8.934 ± .183 x 10^{-5} liter x $moles^{-1}$ x sec^{-1}.*

Table 9. Basic Hydrolysis of Dichlorofluoromethane in Water at 20.35°.

Run B.

No.	t(sec.)	$[CHCl_2F]_o$	Δ ml. N OH^-	$\Delta[OH^-]$	$10^4 k_h$ liter/mole x sec.
1	37825	0.01819	1.590	0.00447	3.939
3	10248	.00907	0.350	.00098	4.311
4	23165	.00581	0.483	.00136	4.315
5	66528	.00639	1.160	.00326	4.126
6	105073	.01238	2.090	.00587	3.805
					4.099 ± .181

$[OH^-]_o$ = 0.0070 M

f = 0.72

Stopped reactions with 10 ml. of 0.1090 N HCl;

blank was 1.41 ml. of 0.2809 N NaOH.

Table 10. Basic Hydrolysis of Dichlorofluoromethane in Water at 20.2°.

Run D. and E.

No.	t(sec.)	$[CHCl_2F]_o$	Δml. N OH^-	$\Delta[OH^-]$	$10^4 k_h$ liter/sec. x mole.
1	13470	0.00997	1.805	0.00119	4.054
3	22235	.01183	3.210	.00211	4.062
4	41420	.01572	5.985	.00394	3.921
5	84857	.01399	7.932	.00522	3.825
6	90360	.01429	8.185	.00539	3.801
					Av.3.933 ± 0.100

No.	t(sec.)	$[CHCl_2F]_o$	Δml. N OH^-	$\Delta[OH^-]$	$10^4 k_h$ liter/sec. x mole.
1	8895	0.01451	1.685	0.00117	3.883
2	16525	.00966	2.090	.00145	4.079
3	46095	.00948	4.625	.00322	4.022
5	67785	.01007	6.111	.00425	3.990
6	87598	.00624	5.280	.00367	4.074
					Av.4.010 ± 0.058

$[OH^-]_o$ = 0.00658 M for run D and 0.00696 M for run E.

f = 0.72

Stopped reactions with 10 ml. of 0.1090 N HCl for run D; blank was 6.625 ml. of 0.0658 N NaOH.

Stopped reactions with 10 ml. of 0.1032 N HCl; blank was 4.835 ml. of 0.0695 N NaOH for run E.

Table 11. Basic Hydrolysis of Dichlorofluoromethane in Water at 20.2°.

Run F.

No.	t(sec.)	$[CHCl_2F]_o$	Δml. N OH^-	$\Delta[OH^-]$	$10^4 k_h$ liter/mole x sec.
5	3642	0.01280	0.716	0.00050	4.301[a]
3	4372	.01259	0.770	.00054	3.939
6	21824	.01181	3.140	.00218	4.037
4	47466	.00923	4.538	.00316	3.915
8	81478	.00904	6.293	.00438	3.926
7	83608	.01138	7.240	.00504	3.927
					Av. 3.949 ± 0.035*

[a]Not averaged (>2.5 average deviation).

$[OH^-]_o$ = 0.00696 M

f = 0.72

Stopped reactions with 10 ml. of 0.1032 N HCl;

blank was 4.835 ml. of 0.06956 N NaOH.

Table 12. Base-catalyzed Deuterium Exchange of Dichlorofluoromethane in Water at 20.2°

Run EA.

$[OH^-]_o$ = 0.00696 M $D_o/(H_o+D_o)$ = 0.6310

m_o = 0.5848

No.	t(sec.)	H_o+D_o	$\Delta[OH^-]$	H+D	D/(H+D)	m	m'
1	9713	0.01327	0.00103	0.01299	0.5543	0.8040	0.6880
2	17329	.00992	.00131	.00957	.4974	1.0105	.7815
3	28603	.01494	.00269	.01422	.4424	1.2605	.8830
6	42572	.01523	.00367	.01424	.3955	1.5288	.9815

$s = s_o(1+13.2y-1913.2y^2)$

No.	b_1	s/s_o[b]	s/s_o[c]	k_1/k_2	a	10^3k_1
1	0.7611	1.0087	1.0116	0.7517	0.1744	2.2643
2	.7653	1.0155	1.0140	.7123	.1604	2.4620
3	.7703	1.0229	1.0215	.6222	.1468	2.6901
6	.7510	1.0223	1.0225	.6398	.1481	2.6664
			Av.	0.6815[d]		

[b]First approximation

[c]Method of least squares

[d]0.6834 by first approximation

$k_1 = 3.949 \times 10^{-4}/a$

$k_1 = 2.5207 \pm 0.1576 \times 10^{-3}$ liter x moles^{-1} x sec^{-1}.

Table 13. Base-catalyzed Deuterium Exchange of Dichlorofluoromethane in Water at 20.2°

Run EG.

$[OH^-]_o$ = 0.00562 M $D_o/(D_o+H_o)$ = 0.6310

m_o = 0.5848

No.	t(sec.)	H_o+D_o	$\Delta[OH^-]$	H+D	D/(H+D)	m	m'
1	11434	0.00767	0.00064	0.00750	0.5520	0.8116	0.6930
2	18280	.00736	.00080	.00715	.5037	.9854	.7690
3	27728	.00966	.00155	.00924	.4593	1.1771	.8476
4	43917	.01629	.00262	.01560	.4758	1.1017	.8165
5	43984	.00740	.00181	.00691	.3921	1.5503	.9851
7	73474	.01095	.00338	.01004	.3441	1.9061	1.1024
6	85305	.01226	.00395	.01110	.3365	1.9719	1.1227

$s = s_o(1+24.3y-4710.5y^2)$.

No.	b_1	s/s_o[b]	s/s_o[c]	k_1/k_2	a	10^3k_1
1	0.7536	1.0104	1.0136	0.9001[e]	0.1825	2.164
2	.7937	1.0234	1.0164	.7340	.1448	2.727
3	.7748	1.0269	1.0264	.6022	.1493	2.645
4	.7544	1.0202	1.0309	.3402[e]	.1661	2.377
5	.7515	1.0295	1.0283	.6680	.1506	2.622
7	.7368	1.0292	1.0284	.6176	.1482	2.665
6	.7304	1.0274	1.0225	.6483	.1500	2.633
				0.6540[d] ± .0376		

[b]First approximation

[c]Method of least squares

[d]0.6639 by first approximation

[e]Not averaged (> 2.5 average deviation)

$k_1 = 3.949 \times 10^{-4}/a$.

$k_1 = 2.548 \pm .158 \times 10^3$ liter x moles^{-1} x sec^{-1}.*

Table 14. Base-catalyzed Deuterium Exchange of Dichloroiodomethane in Water at 0°

Run EI.

$D_o/(H_o+D_o)$ = 0.8511 $(H_o+D_o) \sim 0.01$ M

No.	t (sec.)	H/D	D/(H+D)	$k_1[OH^-] \times 10^7 + k'[NH_3]$
5[a]	410500	0.3482	0.7417	3.3521
7[a]	756080	0.5015	.6660	3.2449
8[a]	1311023	0.8239	.5483	3.3548
3A[a]	2056637	1.3549	.4247	3.3813
1A[a]	2487830	1.7046	.3699	3.3519
				Av. 3.3370 ± 0.0369
2[b]	587711	0.4147	.7069	3.1596
4[b]	876802	0.5612	.6405	3.2425
6[b]	1052590	0.6520	.6052	3.2379
9[b]	1635874	0.9915	.5023	3.2100
10[b]	2299658	1.4980	.4003	3.2806
				Av. 3.2261 ± 0.0330

[a] $[OH^-] = 1.1739 \times 10^{-5}$; $[NH_3] = 0.0281$ N.

[b] $[OH^-] = 1.1582 \times 10^{-5}$; $[NH_3] = 0.0109$ N.

$k_1 = 2.7485 \pm 0.0395 \times 10^{-2}$ sec^{-1} mole^{-1}.*

$k' = 3.9 \pm 2.9 \times 10^{-7}$ sec.$^{-1}$ mole^{-1}.*

Table 15. Base-catalyzed Deuterium Exchange of Dichloroiodomethane in Water at 35.0°

Run EJ

$D_o/(H_o+D_o) = 0.8511$ $(H_o+D_o) \sim 0.01$ M

No.	t (sec.)	H/D	D/(H+D)	$k_1[OH^-] \times 10^5 + k'[NH_3]$
14[a]	3746	0.4375	0.6957	5.3856
11[a]	7491	0.7462	.5727	5.2903
15[a]	10600	1.0689	.4833	5.3345
17[a]	14892	1.5132	.3979	5.1068
16[a]	18295	2.1193	.3206	5.3371
				Av. 5.2908 ± .0739
7[b]	2699	0.3507	.7404	5.1658
5[b]	5424	0.5565	.6425	5.1851
2[b]	7626	0.7331	.5770	5.0973
13[b]	8780	0.8441	.5423	5.1348
12[b]	16270	1.6395	.3789	4.9756
				Av. 5.1117 ± .0602

[a] $[OH^-] = 1.6282 \times 10^{-5}$; $[NH_3] = 0.0278$ N.

[b] $[OH^-] = 1.6064 \times 10^{-5}$; $[NH_3] = 0.0108$ N.

$k_1 = 3.1385 \pm 0.0533$ sec^{-1} $mole^{-1}$*.

$k' = 6.5 \pm 5.7 \times 10^{-5}$ sec^{-1} $mole^{-1}$*.

Table 16. Base-catalyzed Deuterium Exchange of Dibromochloromethane in Water at 0°.

Run EK.

$D_o/(H_o+D_o) = 0.9299$ $(H_o+D_o) \sim 0.009$ M

No.	t (sec.)	H/D	D/(H+D)	$k_1 [OH^-] + k' [NH_3]$ x 10^6
3[a]	269869	0.6966	0.5895	1.6897
8[a]	352044	0.9448	.5142	1.6832
6[a]	436119	1.2108	.4523	1.6526
2[a]	517882	1.5309	.3951	1.6530
11[a]	556361	1.6900	.3718	1.6482
				Av. 1.6653 ± 0.0169
16[b]	224289	0.5508	.6448	1.6326
9[b]	313017	0.7881	.5593	1.6246
10[b]	424149	1.1255	.4705	1.6066
4[b]	479928	1.3204	.4310	1.6026
7[b]	598879	1.8056	.3564	1.6015
				Av. 1.6136 ± 0.0120

[a] $[OH^-] = 1.1527 \times 10^{-5}$; $[NH_3] = 0.0277$ N.

[b] $[OH^-] = 1.1215 \times 10^{-5}$; $[NH_3] = 0.0106$ N.

$k_1 = 1.4350 \pm 0.0159 \times 10^{-1}$ sec.$^{-1}$ mole^{-1}.*

$k' = 4.1 \pm 12.4 \times 10^{-7}$ sec^{-1}. mole^{-1}.*

Table 17. Base-catalyzed Deuterium Exchange of Dibromochloromethane in Water at 35.0°.

Run EL.

$D_o/(H_o+D_o) = 0.9299$ $(H_o+D_o) \sim 0.009$ M

No.	t (sec.)	H/D	D/(H+D)	$k_1[OH^-] + k'[NH_3]$ x 10^4
2[a]	1396	0.4784	0.6764	2.2802
5[a]	1985	0.6738	.6014	2.2290
12[a]	2699	0.9786	.5054	2.2594
4[a]	3735	1.4443	.4091	2.1987
3[a]	6631	3.5616	.2193	2.1795
				Av. 2.2294 ± 0.0324
10[b]	1632	0.5405	.6491	2.2025
6[b]	2210	0.7478	.5721	2.1980
15[b]	3178	1.1530	.4645	2.1846
7[b]	5204	2.2695	.3059	2.1371
8[b]	7253	3.8491	.2062	2.0769
				Av. 2.1598 ± 0.0423

[a] $[OH^-] = 1.5987 \times 10^{-5}$; $[NH_3] = 0.0274$ N.

[b] $[OH^-] = 1.5554 \times 10^{-5}$; $[NH_3] = 0.0104$ N.

$k_1 = 13.8478 \pm 0.3463$ sec^{-1}. mole^{-1}.*

$k' = 5.7 \pm 32.0 \times 10^{-5}$ sec.$^{-1}$ mole^{-1}.*

Table 18. Basic Hydrolysis of Bromochlorofluoromethane in Water at 0°

Run O. and P.

No.	t(sec.)	$[CHBrClF]_o$	Δml. N OH^-	$\Delta[OH^-]$	$10^2 k_h$ liter/sec. x mole.
9	1692	0.00914	0.602	0.00035	1.1703[a]
8	2550	.00976	0.972	.00056	1.1988[a]
7	5217	.01065	2.177	.00126	1.3112
6	8772	.01025	3.177	.00184	1.2786
5	10797	.00902	3.462	.00200	1.3225
3	13531	.00862	3.972	.00230	1.3294
				Av.	1.3104 ± .0159

No.	t(sec.)	$[CHBrClF]_o$	Δml. N OH^-	$[OH^-]$	$10^3 k_h$ liter/sec. x mole.
9	3809	0.01000	1.490	0.00182	1.2274[a]
8	5871	.01074	2.500	.00305	1.3442
5	10560	.01060	3.810	.00465	1.3005
7	14069	.00935	4.340	.00530	1.3457
6	18549	.00961	5.215	.00637	1.3160
3	21600	.00957	5.635	.00688	1.2938
				Av.	1.3201 ± .0199*

[a]Not averaged (>2.5 of average deviation); f = 0.629

$[OH^-]_o$ = 0.00579 M for run O and 0.01196 for run P.

Stopped reactions with 5 ml. of 0.1316 N $HClO_4$;

blank was 3.093 ml. of 0.0520 N NaOH for run O.

Stopped reactions with 10 ml. of 0.1316 N $HClO_4$;

blank was 2.220 ml. of 0.1099 N NaOH for run P.

Table 19. Base-catalyzed Deuterium Exchange of Bromochlorofluoromethane in Water at 0°

Run EQ.

$[OH^-]_o$ = 0.01712 M $D_o/(H_o+D_o)$ = 0.9598

m_o = 0.0428

No.	t(sec.)	H_o+D_o	$\Delta[OH^-]$	H+D	D/(H+D)	m	m'
11	4719	0.00905	0.00193	0.00852	0.8646	0.1566	0.0973
9	7542	.00996	.00323	.00907	.8261	.2105	.1221
5	9306	.01200	.00465	.01072	.8084	.2447	.1374
8	10991	.00962	.00437	.00841	.7817	.2793	.1526
7	16291	.00896	.00577	.00738	.7282	.3733	.1925
6	22717	.00928	.00756	.00719	.6832	.4638	.2281
3	27004	.00967	.00871	.00727	.6575	.5209	.2506

$s = s_o(1+4.7y-1733.7y^2)$

No.	b_1	s/s_o[b]	s/s_o[c]	k_1/k_2	a	10^3k_1
11	0.5949	1.0053	1.0026	0.5645	0.6029	2.1896
9	.5671	0.9979	0.9971	.5621	.6213	2.1247
5	.5578	.9937	.9844	.5866	.6210	2.1258
8	.5450	.9868	.9875	.5759	.6256	2.1101
7	.5074	.9599	.9694	.5827	.6421	2.0559
6	.4766	.9298	.9364	.5777	.6519	2.0250
3	.4657	.9154	.9095	.5737	.6474	2.0391
				Av.0.5747[d] ± .0068		2.0957

[b]First approximation

[c]Method of least squares

[d]0.5733 by first approximation

k_1 = 1.3201 x 10^{-3}/a.

k_1 = 2.0957 ± .0478 x 10^{-3} liter x $moles^{-1}$ x sec^{-1}.*

Table 20. Basic Hydrolysis of Bromochlorofluoromethane in Water at 15°.

Run M.

No.	t(sec.)	$[CHBrClF]_o$	Δml. N OH^-	$\Delta[OH^-]$	$10^2 k_h$ liter/sec. x mole.
8	1202	0.01305	8.372	0.00578	1.5750[a]
7	2235	.01435	11.777	.00812	1.5090[a]
6	2801	.01455	12.772	.00881	1.5053
3	3600	.01522	13.557	.00935	1.4017
5	4240	.01346	13.737	.00948	1.4662
9	4774	.01296	13.717	.00946	1.3463

[a]Only values used as other points were beyond 75 per cent used.

$[OH^-]_o$ = 0.01023 M.

f = 0.625

Stopped reactions with 5 ml. of 0.1316 N $HClO_4$.

Blank was -4.868 ml. of 0.0655 N NaOH.

Table 21. Basic Hydrolysis of Bromochlorofluoromethane in Water at 15°

Run N.

No.	t(sec.)	$[CHBrClF]_o$	Δml. N OH^-	$[OH^-]$	$10^2 k_h$ liter/sec. x mole.
8	756	0.00695	2.325	0.00169	1.5068
9	912	.00771	3.010	.00219	1.5368
7	1202	.00934	4.290	.00312	1.5302
6	1803	.00915	5.390	.00392	1.4754
5	2415	.01035	6.705	.00488	1.4324
3	3284	.00852	6.955	.00506	1.4099
					1.4969[a] ± .0430*

[a]Average includes Nos. 7 and 8 from run M.

$[OH^-]_o$ = 0.0070 M.

f = 0.625

Stopped reactions with 5 ml. of 0.1316 N $HClO_4$;

Blank was 0.350 ml. of 0.0655 N NaOH.

Table 22. Base-catalyzed Deuterium Exchange of Bromochlorofluoromethane in Water at 15.0°

Run ER

$[OH^-]_o$ = 0.08544 M $D_o/(H_o+D_o)$ = 0.9589

m_o = 0.0428

No.	t(sec.	H_o+D_o	$[OH^-]$	H+D	D/(H+D)	m	m'
11	900	0.00770	0.00170	0.00723	0.8694	0.1502	0.0944
10	1460	.00921	.00303	.00838	.8360	.1962	.1161
9	1709	.00672	.00266	.00599	.8152	.2268	.1298
8	2009	.00947	.00405	.00835	.8131	.2299	.1308
3	2552	.01122	.00512	.00981	.7986	.2522	.1405
7	2846	.00829	.00459	.00702	.7735	.2928	.1578
6	3165	.00897	.00510	.00756	.7689	.3006	.1615
5	3600	.00764	.00501	.00626	.7443	.3436	.1794

$s = s_o(1+2.6y-1352.8y^2)$

No.	b_1	s/s_o[b]	s/s_o[c]	k_1/k_2	a	10^2k_1
11	0.5728	0.9958	0.9917	0.5754	0.6245	2.3971
10	.5442	.9848	.9797	.5883	.6458	2.3181
9	.5319	.9774	.9836	.5846	.6507	2.3006
8	.5125	.9688	.9673	.6155	.6767	2.2122
3	.5175	.9685	.9512	.5852	.6608	2.2654
7	.4973	.9533	.9596	.5964	.6726	2.2257
6	.4956	.9513	.9516	.5830	.6716	2.2290
5	.4824	.9377	.9531	.5880	.6730	2.2244
			Av.	0.5896[d] ± .0083		2.2716

[b]First approximation

[c]Method of least squares

[d]0.5909 by first approximation

$k_1 = 1.497 \times 10^{-2}/a.$

$k_1 = 2.2716 \pm .0503 \times 10^{-2}$ liter x moles^{-1} x sec^{-1}.*

Table 23. Values of $\underline{f}$ Determined for Dichlorofluoromethane

Run	Moles[a] of Base Used X 10^3	Moles $AgNO_3$ Added X 10^3	Moles KSCN Added X 10^3	Moles of Cl^- X 10^3	$\underline{f}$
A	42.14	24.76	2.64	22.15	0.805
B	28.09	15.48	0.27	7.61	0.694
C	14.08	9.28	1.71	7.57	0.714
D	7.02	4.33	0.58	3.75	0.745
E	4.21	2.48	0.21	2.27	0.721
F	4.21	2.48	0.21	2.27	0.725
G	4.21	2.48	0.21	2.27	0.719
H	42.14	24.76	2.11	22.65	0.720
					Av. 0.720[b]

[a]Molar concentration in base was four times moles of base used.

[b]Excluded run A in average (>2.5 average deviation)

Table 24. Summary of Kinetic Data.

$CHCl_2F$	0°	20.2°	$\Delta H^{\ddagger}$(kcal.)	$\Delta S^{\ddagger}$(e.u.)
10^4k_h	0.1234 ± .0010	3.949 ± .035	26.8 ± 0.2	17.1 ± 0.5
10^4k_1	0.8934 ± .0183	25.48 ± 1.58	25.9 ± 0.6	17.7 ± 2.3
10^4k_2	1.574 ± .032	38.78 ± 2.40	24.7 ± 0.6	14.6 ± 2.3
k_1/k_2	0.568 ± .009	0.654 ± .040		

$CHCl_2I$	0°	35°	$\Delta H^{\ddagger}$(kcal.)	$\Delta S^{\ddagger}$(e.u.)
10^4k_1	274.85 ± 3.95	31385 ± 533	22.1 ± 0.2	15.3 ± 0.5
10^4k_2[a]	481.27 ± 6.92	46827 ± 796	21.3 ± 0.2	13.6 ± 0.5
$10^4k'$	0.0039 ± .0029	0.651 ± .567		
k_2/k_1[b]	1.751	1.4920		

$CHBr_2Cl$	0°	35°	$\Delta H^{\ddagger}$(kcal.)	$\Delta S^{\ddagger}$(e.u.)
10^4k_1	1435.0 ± 15.8	138478 ± 3463	21.3 ± 0.2	15.6 ± 0.6
10^4k_2[a]	2512.7 ± 27.8	20661 ± 5167	20.5 ± 0.2	14.0 ± 0.6
$10^4k'$	0.004 ± .012	0.57 ± 3.20		
k_2/k_1[b]	1.751	1.4920		

CHBrClF	0°	15°	$\Delta H^{\ddagger}$(kcal.)	$\Delta S^{\ddagger}$(e.u.)
10^4k_h	13.20 ± 0.20	149.69 ± 4.30	28.8 ± 0.5	19.2 ± 1.7
10^4k_1	20.96 ± 0.48	227.16 ± 5.03	24.3 ± 0.5	18.4 ± 1.7
10^4k_2	36.47 ± 0.83	385.26 ± 8.53	24.1 ± 0.5	18.5 ± 1.7
k_1/k_2	0.575 ± .007	0.590 ± .008		

[a]Used isotope effect average from dichlorofluoromethane and bromochlorofluoromethane x k_1

[b]Average isotope effect from dichlorofluoromethane and bromochlorofluoromethane.

Table 25. Apparent Molecular Extinction Coefficients for Deuterohaloforms and Protohaloforms.

Wave[a] Length	Slit Control	ϵ_{CHX_3} [b]	ϵ_{CD_3} [b]
$CHCl_2F$			
9.415	144	393 ± 2	220 ± 2
10.637	181	1.5 ± 0.2	420 ± 3
12.635	275	516 ± 2	-0.05 ± 0.1
13.290	330.5	26 ± 2	392 ± 5
$CHCl_2I$			
8.845	124	159.6 ± 2.1	-1.7
11.117	195.5	0.28 ± 0.01	153.9 ± 1.5
11.866	228	-0.04 ± 0.00	282.1 ± 3.1
13.217	324	343.1 ± 3.2	-0.085
$CHBr_2Cl$			
8.730	120	118.5 ± 1.5	-0.63
11.263	201	-0.5 ± 0.0	177.5 ± 0.8
11.717	220	-0.7 ± 0.1	234.2 ± 1.0
13.346	342	299.3 ± 2.4	3.9
CHBrClF			
9.399	140.5	433.3 ± 3.1	261.2 ± 2.0
10.983	190	0.	315.9 ± 2.6
12.882	290	504.6 ± 2.3	-0.07
13.491	347	0.	255.3 ± 4.7

[a]All runs at ~965 resolution, gain 5 and response of 4: used 0.0510 cm. solution cell and 0.0506 solvent cell.

[b]First four were determined in carbon disulfide and all others were determined in isooctane.

APPENDIX 2

DERIVATIONS

Equation for the Rate of Deuterium Exchange with Concomitant Hydrolysis.--For a solution containing a mixture of protohaloform, deuterohaloform and base the following kinetic equations were formulated in terms of the reaction mechanism

$$CDX_3 + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CX_3^- + HOD$$

$$CHX_3 + OH^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} CX_3^- + H_2O$$

$$CX_3^- \xrightarrow{k_3} CX_2 + X^-$$

where X = any halogen. Then treating k_{-2} as a first-order rate constant since $[H_2O]$ remains almost constant and neglecting $[DOH]$ return as there are $\sim 10^4$ times as many protons in water as deuterons in the deuterohaloform, it can be seen that

$$-dD/dt = k_1BD$$

$$-dH/dt = k_2BH - k_{-2}I$$

where D = $[CDX_3]$, H = $[CHX_3]$, B = $[OH^-]$ and I = $[CX_3^-]$. A steady-state assumption gives

$$dI/dt = 0 = k_1BD + k_2BH - k_{-2}I - k_3I$$

$$I = \frac{B(k_1D+k_2H)}{k_3 + k_{-2}}$$

then by division the following is obtained

$$\frac{dH}{dB} = \frac{k_2H}{k_1D} - \frac{k_{-2}I}{k_1BD}$$

and by substitution for I

$$\frac{dH}{dD} = \frac{k_2H}{k_1D} - \frac{k_{-2}(k_1D+k_2H)}{k_1(k_3+k_{-2})D}$$

which can be arranged to give

$$\frac{dH}{dD} = \frac{k_2k_3}{k_1(k_3+k_{-2})}\frac{H}{D} - \frac{k_{-2}}{k_3+k_{-2}}$$

Let the following terms be defined as

$$r = \frac{k_3}{k_{-2}};\ b = \frac{1}{1-r};\ \frac{k_2k_3}{k_3+k_{-2}} = k_h \text{ (hydrolysis) } CHX_3$$

$$a = \frac{k_h}{k_1}$$

then by substitution

$$\frac{dH}{dD} = \frac{k_h}{k_1}\frac{H}{D} - \frac{1}{1+r}$$

which can also be expressed as

$$\frac{dH}{dD} = a\frac{H}{D} - b$$

If $H/D = m$, then $dH = mdD + Ddm$ and

$$\frac{dH}{dD} = m + D\frac{dm}{dD};\ m + D\frac{dm}{dD} = am - b$$

$$d\ln D = \frac{dm}{(a-1)m - b} = \frac{-dm}{(1-a)m + b}$$

which may be integrated between the limits m_o and m, and D_o and D

$$c = (1-a)\ln D_o + \ln\left[(1-a)m_o + b\right]$$

$$c = (1-a)\ln D + \ln\left[(1-a)m + b\right]$$

$$(1-a)\ln D_o + \ln\left[(1-a)m_o + b\right] = (1-a)\ln D + \ln\left[(1-a)m + b\right]$$

$$\ln\left[(D_o/D)^{1-a}\right] = \ln\frac{\left[(1-a)m + b\right]}{\left[(1-a)m_o + b\right]}$$

$$b = \frac{(1-a)\left[m-(D_o/D)^{1-a}\ m_o\right]}{(D_o/D)^{1-a} - 1}$$

Since

$$a = \frac{k_2k_3}{k_1(k_3+k_{-2})} = \frac{k_2k_3}{k_1(k_{-2}/b)}; \quad \frac{k_3}{k_{-2}} = \frac{1}{b} - 1$$

$$a = \frac{k_2 b}{k_1} \left(\frac{1}{b} - 1\right)$$

then

$$a = \frac{k_2}{k_1} (1-b)$$

where k_2/k_1 = isotope effect. Since it was seen that $(k_2k_3/k_3+k_{-2}) = k_h$, then, $a = k_h/k_1$.

Equations for the Calculation of the Isotope Effect.--For these derivations the same symbols and reaction mechanism are used as in the proceeding derivations. If $y = B_o - B$ (amount of base used) and $y/(3+f)$ = total haloform lost by hydrolysis, the following can be seen

$$dy/dt = k_3(3+f)I$$

and substituting for I

$$\frac{dy}{dt} = \frac{(3+f)k_3\left[k_1D+k_2H\right] B}{k_3+k_{-2}}$$

If k_h (hydrolysis rate constant for protohaloform) =

k_2k_3/k_3+k_{-2}, the following can be seen

$$dy/dt = (3+f)\left[k_1/k_2D+k_hH\right](B_o-y)$$

Over a small part the reaction (3+f) (k_hD+k_hH) does not vary much and therefore, let the expression equal $\underline{s}$ (a constant)

$$dy/dt = s(B_o-y)$$

which yields upon integration

$$-\ln(B_o-y) = st + c$$

and on evaluation of $\underline{c}$ with $y = 0$, $t = 0$

$$s = \frac{2.303}{t} \log \frac{B_o}{B_o-y}$$

If $\underline{s}$ at $\underline{t}$ time is expressed in terms of $\underline{s_o}$ and $\underline{y}$ by the equation

$$s = s_o(1+vy-ny^2)$$

where $\underline{s_o}$ is for $\underline{t} = 0$ and choosing the optimum values of $\underline{v}$ and $\underline{n}$ by the method of least squares. The sums of the squares of the deviation are

$$\sum_i \left[(s/s_o)_i-1-vy_i+ny_i^2\right]^2$$

If the partial with respect to v is taken, the following is obtained

$$\sum_i \left[(s/s_o)_i y_i - y_i - v y_i^2 + n y_i^3 \right] = 0$$

and the partial with respect to n yields

$$\sum_i \left[(s/s_o)_i y_i^2 - y_i^2 - v y_i^3 + n y_i^4 \right] = 0$$

solve for v and n. By substituting above for s, the following is obtained

$$s_o dt = \frac{dy}{(1+vy-ny^2)\ (B_o-y)}$$

which can be divided into parts in order to integrate

$$\frac{1}{(1+vy-ny^2)(B_o-y)} = \frac{Cy+C_3}{(1+vy-ny^2)} + \frac{C_2}{B_o-y}$$

where

$$C = -\frac{n}{1+vB_o-nB_o^2}$$

$$C_3 = \frac{v-nB_o}{1+vB_o-nB_o^2}$$

$$C_2 = \frac{1}{1+vB_o-nB_o^2}$$

yielding

$$s_o dt = C \int \frac{y\,dy}{1+vy-ny^2} + C_3 \int \frac{dy}{1+vy-ny^2} + C_2 \int \frac{dy}{B_o-y}$$

which if taken by parts gives

$$C\int \frac{y\,dy}{1-ny^2+vy} = C\left[\frac{1}{-2n}\ln(-ny^2+vy-1) - \frac{v}{-2n}\int \frac{dy}{-ny^2+vy+1}\right]$$

$$C_3 \int \frac{dy}{-ny^2+vy+1} = C_3 \left[\frac{1}{\sqrt{v^2+4n}}\ln \frac{-2ny+v-\sqrt{v^2+4n}}{-2ny+v+\sqrt{v^2+4n}}\right.$$

$$C_2 \int \frac{dy}{B_o-y} = -C_2 \ln(B_o-y)$$

Since $C = -nC_2$, $C_3 = (v-nB_o)C_2$ and $C_2 = 1/(1+vB_o-nB_o^2)$, upon substitution

$$s_o t = 1.15C_2 \log (1+vy-ny^2) + (v/2-nB_o)C_2 \frac{2.303}{\sqrt{v^2+4n}} \cdot$$

$$\log \frac{-2ny+v-\sqrt{v^2+4n}}{-2ny+v+\sqrt{v^2+4n}} \quad -2.303C_2 \log(B_o-y) - c$$

evaluating c, the final expression is obtained

$$s_o t = 2.303C_2 \log \frac{B_o\sqrt{1+vy-ny^2}}{B_o-y} + \frac{2.303C_2\left[(v/2)-nB_o\right]}{C_1}.$$

$$\log \frac{(v-2ny-C_1)(v+C_1)}{(v-2ny+C_1)(v-C_1)}; \text{ where } C_1 = \sqrt{v^2+4n}$$

Proof.--The following argument shows that where k_h is negligible in comparison to k_1, the values of the rate constants obtained are completely independent of the assumption that the deuterium compounds ($CDCl_2I$ and $CDBr_2Cl$) do not absorb at the protium maximum[a].

Let p/r be designated as the calculated fraction of deuteration of haloform, p equal the true value (fraction) and ϵ_{CDX_3} equal calculated extinction coefficient. Since p/r and ϵ_{CDX_3} are obtained from measurements on samples of known total haloform concentration (C), the following relation to optical density (O.D.) can be seen

$$O.D. = 1 \left[p/r \; \epsilon_{CDX_3 C} + (1-p/r) \; \epsilon_{CHX_3 C} \right]$$

O.D. can also be expressed in terms of $\epsilon_{CDX_3}^*$ (true extinction coefficient for deuterohaloform) for a deuterohaloform

$$O.D. = 1 \left[p \, \epsilon_{CDX_3 C}^* + (1-p) \, \epsilon_{CHX_3 C} \right]$$

Since O.D. is constant for a given concentration of haloform

---

[a]In the cases where k_h is comparable to k_1 this assumption for deuterobromochlorofluoromethane could not be more than 4 per cent in error but for deuterodichlorofluoromethane this could lead to a much larger error. However, if the actual deuterium content of dichlorofluoromethane had been greater than 63.1 per cent, drifting rate constants would have been obtained.

mixture, $\underline{r}$ can be solved for

$$r = \frac{\epsilon CDX_3 - \epsilon CHX_3}{\epsilon CDX_3^* - \epsilon CHX_3}$$

This ratio indicates that $\underline{r}$ is a constant which is independent of the haloform concentration and of $\underline{p}$. In the equation for k_1 (p. 29) where $k_1 >>> k_h$, the following expression was used

$$\log(p_o + p_o H/D)$$

which is also the same as $\log(p_o/p)$. In our determinations

$$\log = \frac{(p_o/r)}{(p/r)}$$

which was used and they are identical.

Spectrum Information

Spectrum data are available in the literature for $CHCl_2F$[1], $CHBr_2Cl$[2], $CDBr_2Cl$[2], $CHBrClF$[3] and CHF_3[4]. The following four pages show the individual infrared spectrum of the protium and mixed protium-deuterium compounds of each haloform which were used in the kinetic measurements.

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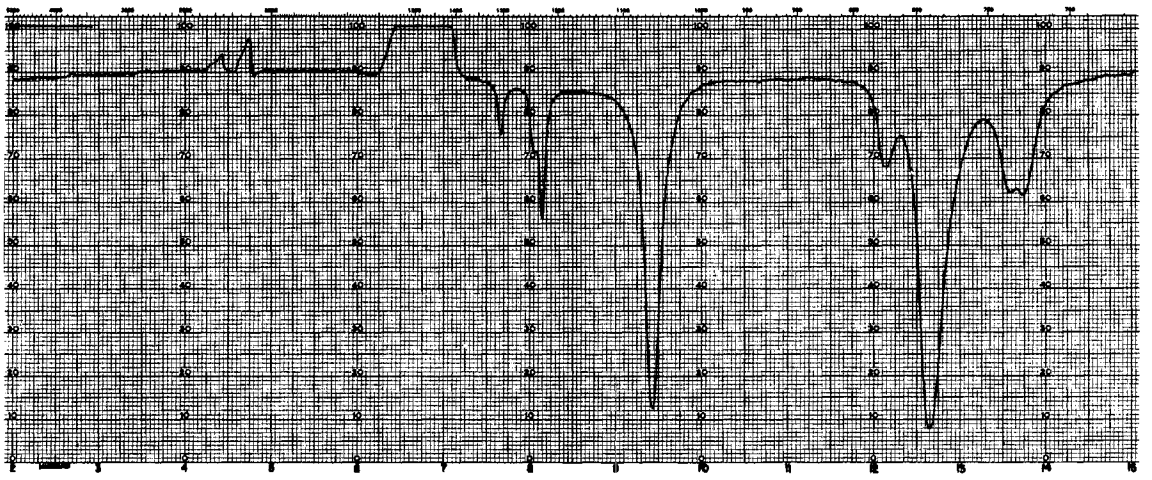
(1). E. K. Plyler and W. S. Benedict, J. Res. Bur. Stand., 47, 202 (1951).

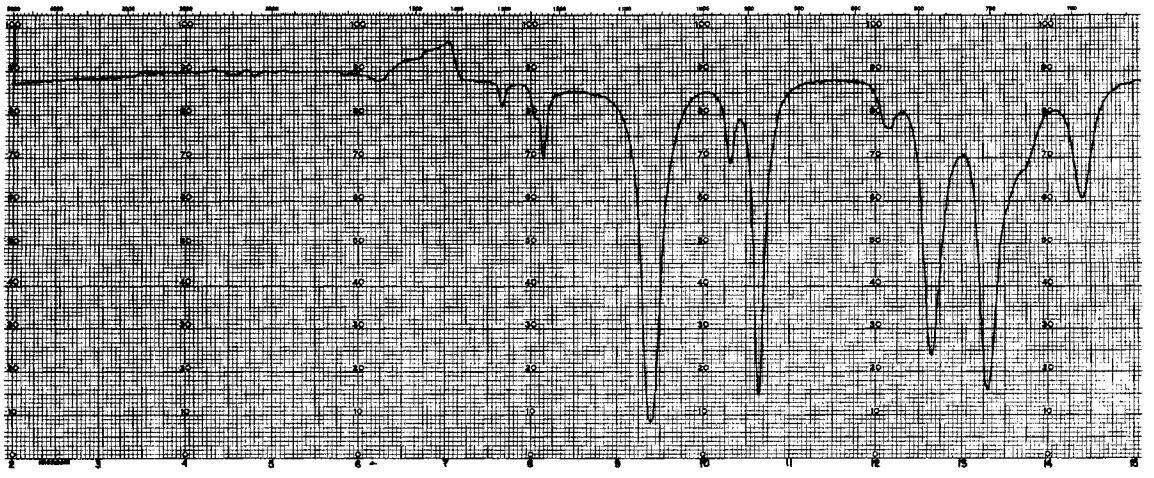
(2). D. A. Pontarelli, A. G. Meister, F. F. Cleveland, F. L. Voelz, R. B. Bernstein and R. H. Sherman, J. Chem. Phys., 20, 1949 (1952).

(3). E. K. Plyler and M. A. Lamb, J. Res. Bur. Stand., 46, 382 (1951).

(4). G. Herzberg and H. J. Bernstein, J. Chem. Phys., 16, 30 (1948).

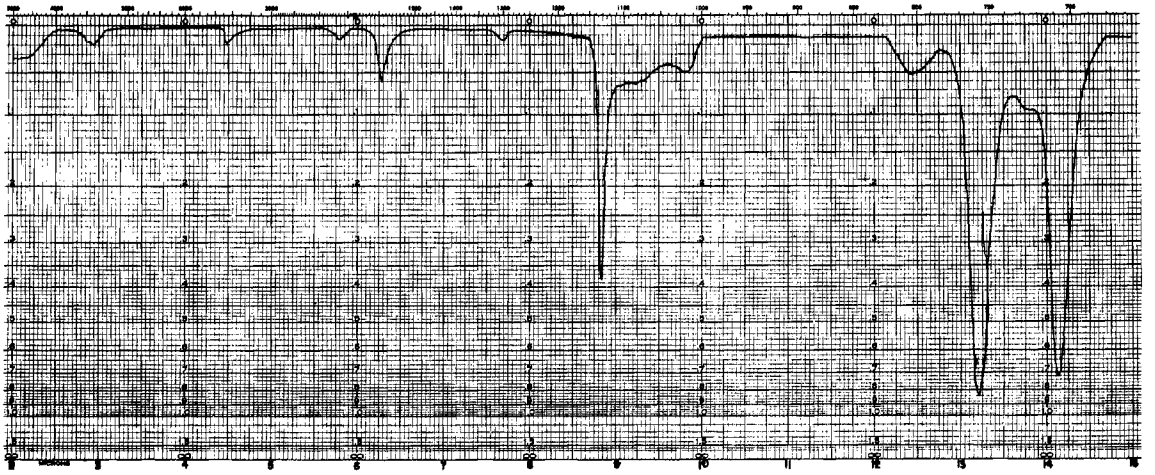


$CHCl_2F$ in CS_2 ~ 0.02 M.

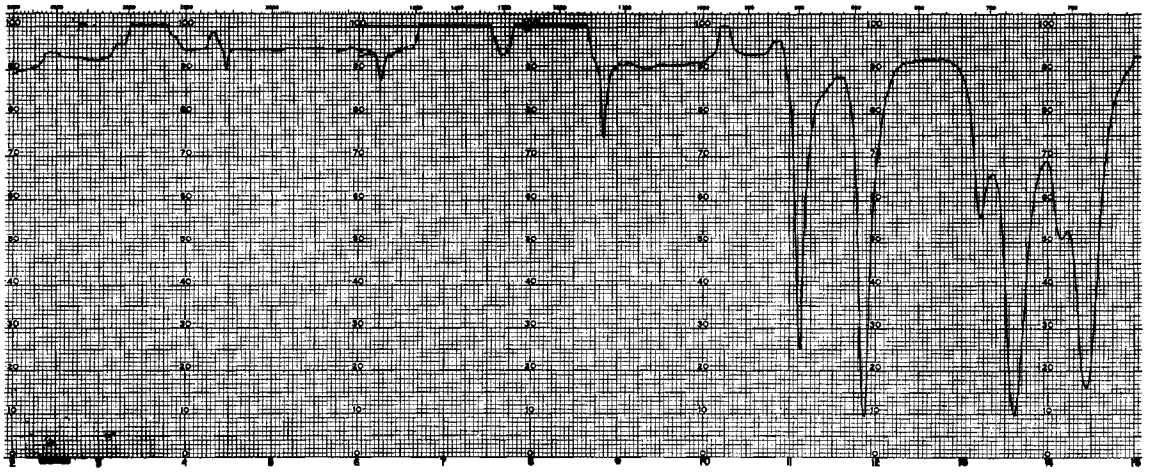


$CDCl_2F$ – $CHCl_2F$ in CS_2 ~ 0.025 M.

Figure 4.

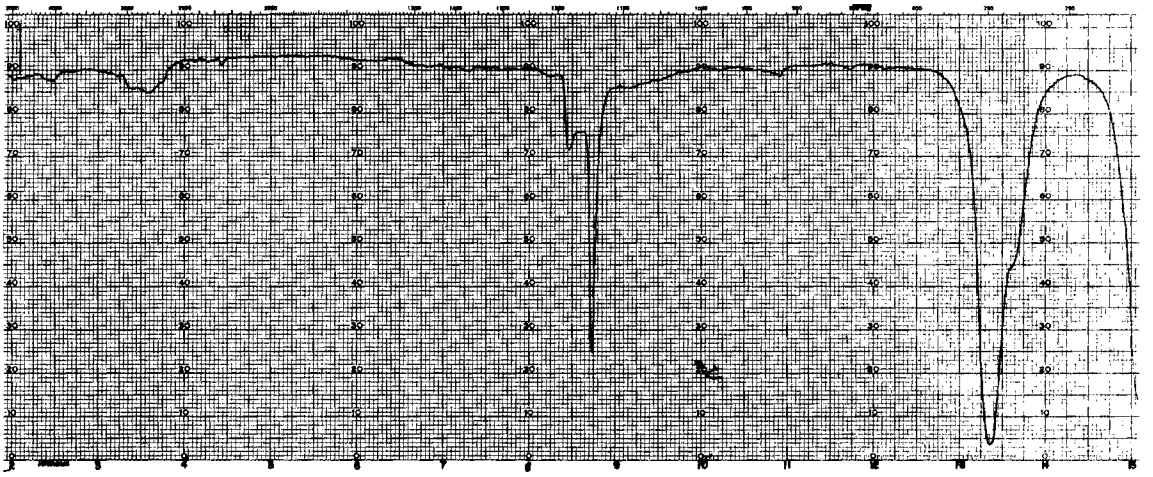


$CHCl_2I$ in Isooctane ~ 0.04 M.

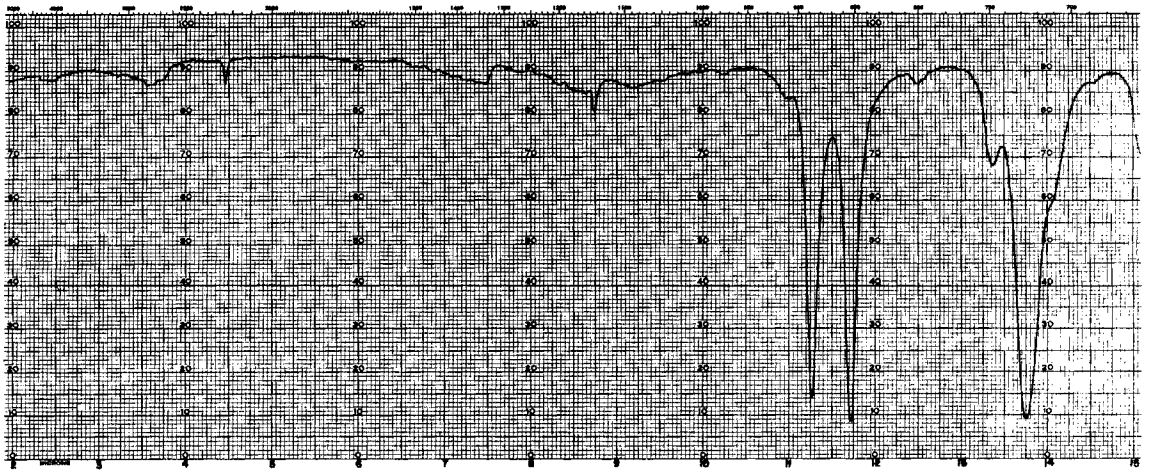


$CDCl_2I$ – $CHCl_2I$ in Isooctane ~ 0.045 M. $CDCl_2I$

Figure 5.

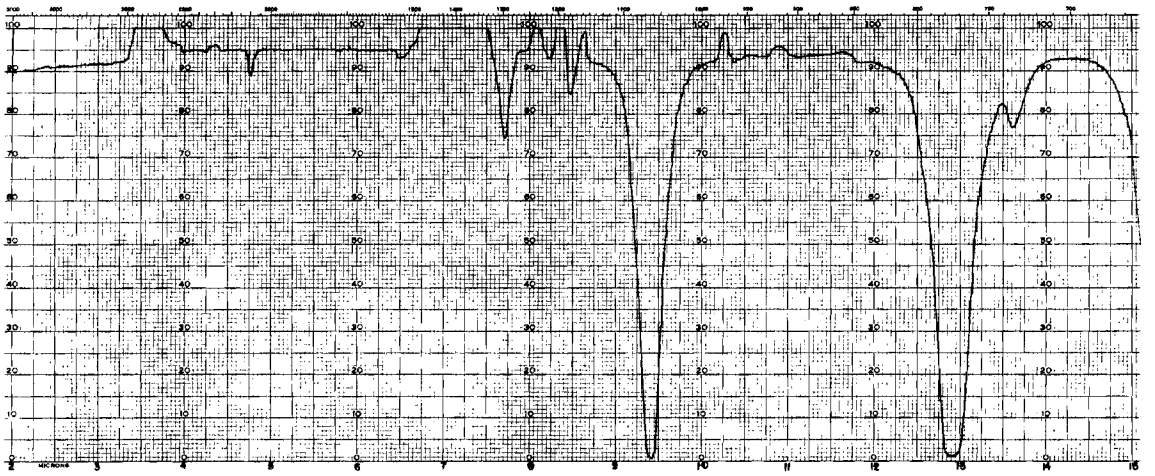


$CHBr_2Cl$ in Isooctane ~ 0.06 M.

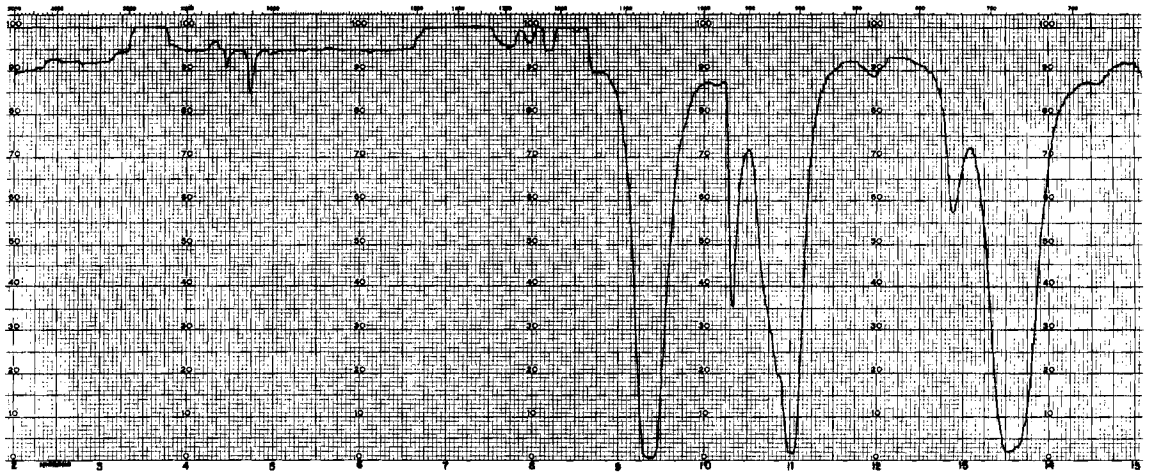


$CDBr_2Cl$ – $CHBr_2Cl$ in Isooctane ~ 0.06 M. $CDBr_2Cl$

Figure 6.



CHBrClF in Isooctane ~ 0.13 M.



CDBrClF – CHBrClF in Isooctane ~ 0.13 M. CDBrClF

Figure 7.

Table 26. Absorption Bands for Fluoroform and Deuterofluoroform

SOURCE CHF_3-CDF_3			
Du Pont[a]	Laboratory[b]	Literature[c]	Laboratory[d]
Microns	Microns	Microns	Microns
3.3----stg.	3.3----stg.	3.3----stg.	2.9----w.
5.7----w.	7.5----stg.	8.2----m.	7.3----v. stg.
7.3----stg.	8.5----stg.	14.2---m.	8.2----stg.
8.4-8.8--v.stg.	8.7----stg.	7.4----stg.	8.7----stg.
8.2----w.	8.2----w.	8.7----v.stg.	9.1----w.
10.7---w.	12.3---m.		9.7----stg.
11.8---m.	13.9---w.		10.2---stg.
13.8---stg.			10.4---m.
			11.6---w.
			12.5---m.
			13.8---m.

[a]Du Pont Commercial CHF_3 at 10 - 125 mm. of CHF_3.

[b]Laboratory prepared CHF_3 (From CF_3CO_2Na + NaOH) at 170 mm. of CHF_3.

[c]Herzberg and Bernstein[4] literature.

[d]Laboratory prepared CDF_3 (from CF_3CO_2Na + NaOH) at 200 - 675 mm. CDF_3.

Absorption Strength:

w. = weak

m. = medium

stg. = strong

v. stg. = very strong

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